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CHARACTERIZATION OF ORGANOMETALLIC POLYMERS BY CHROMATOGRAPHIC METHODS AND NUCLEAR MAGNETIC RESONANCE

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Abstract

Continuing research into the analytical methodology for characterization of organometallic polymers (OMPs) has produced improved methods of characterization by size exclusion chromatography (SEC) and Fourier transform nuclear magnetic resonance (FTNMR). Molecular weight (MW) and MW dispersion (MWD), as well as the amount of tin associated with fractions of various MW can now be reliably determined by SEC coupled with various detectors: differential refractive index (ΔRI), ultra-violet (UV), and graphite furnace atomic absorption (GFAA) spectroscopy. Configurational sequencing in terms of both tacticity and sequencing of monomer units can be determined by FTNMR, as well as certain tin-containing impurities. Removal of tributyltin groups to produce a metal-free copolymer allows much more informative FTNMR spectra to be obtained. All of the polymers examined are approximately 80 percent racemic (r) and 20 percent meso (m) in tacticity (i.e., predominantly syndiotactic). The growing chain end in the copolymer adds either of the monomer units approximately in proportion to its instantaneous concentration in the mixture (i.e., at random).

1.0 Introduction

In previous communications from this laboratory [1,2] we have described the nature of the problems involved in the characterization of organometallic copolymers (OMPs) and the methods of molecular characterization, by size exclusion chromatography (SEC) and Fourier transform nuclear magnetic resonance (FTNMR), currently under development. The present report answers several questions arising from our previous research and provides the basis for using complementary molecular characterization methods as a part of a Mil-Spec to assure the Navy of practical criteria for evaluating commercially synthesized OMPs for use in controlled-release coatings on ships.

Earlier reports have dealt with materials prepared by the free-radical-induced copolymerization of methyl methacrylate (MMA) and tributyltin methacrylate (TBTM) at the temperature of refluxing benzene [3]. We have been primarily concerned with two candidate OMPs: one, identified as OMP-2, contains a 1:1 mole ratio of MMA to TBTM; while the second, identified as OMP-8, contains a 2:1 ratio of the respective monomers. Samples prepared by the David Taylor Naval Ship Research and Development Center (DTNSRDC) using this method are hereinafter identified as OMP-2N and OMP-8N. A new process, proposed for commercial development, involves preparation of a "pre-polymer" of MMA and methacrylic acid (MAA) by free-radical-induced copolymerization followed by esterification of the pendant free acid groups on the pre-polymer by bis-tributyltin oxide (TBTO). We have examined commercial OMPs of the same nominal composition as above, which are identified in this report as OMP-2P and OMP-8P. We have also examined the pre-polymer before reaction with TBTO.

1.1 Complementary Nature of SEC and NMR

Size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) are complementary techniques involved in organometallic copolymer characterization. SEC is coupled with various detectors: graphite furnace atomic absorption spectroscopy (GFAA), differential refractive index (ΔRI), and ultraviolet spectroscopy (UV). SEC-GFAA is capable of dealing with exceedingly small samples [4]. With samples of 5 mg or less, SEC provides characterization of a copolymer sample according

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to its molecular weight (MW), molecular weight distribution (MWD), and the distribution of metal (specifically tin) among fractions of different MW. SEC, in tandem with the detectors used at NBS, is capable of detecting solvent impurities and side reaction products. The SEC method is, however, not at all sensitive to configurational sequencing of the polymer. The complementary technique of NMR requires substantially larger samples of (greater than one gram for non-proton NMR). It provides configurational sequencing information [5] which is complete at the triad level in the specific case of copolymers of MMA and TBTM. It also gives information regarding tin-containing impurities. The NMR method is affected only in the crudest way by MW, and does not provide a useful way to estimate MW.

1.2 Limitations

Each of these methods has its own special strengths and limitations. SEC requires adequate standards to be able to provide absolute MW information. These are not yet available for the methacrylate copolymers under consideration here. However, comparative results are attained and are very useful, so long as suitable reference material can be made available. NMR is valuable for determining molecular structures, but it is not a trace method and is not well suited to determine, or to characterize with certainty, small amounts of impurities. The smallest amount of an impurity detectable by NMR is dependent on many factors: (1) whether the impurity signal is well separated from all other signals; (2) the linewidth of the impurity signal--small molecules generally have inherently narrow lines and are consequently easier to see at low concentrations; (3) the amount of time available for running a spectrum--since the signal-to-noise ratio increases at best only as the square root of the time, the point of diminishing returns is usually reached in an overnight scan of about 16 hours. Taking all of these factors into account, it is usually possible to detect impurities at the 1 percent level if their signals are well separated from all other peaks and usually not possible to detect 0.1 percent of impurity except in extraordinarily favorable cases.

2.0 Apparatus and Materials*

2.1 SEC

2.1.1 Chemicals

Benzene, tetrahydrofuran (THF), methanol, methyl isoamyl ketone, acetic acid and other common solvents were all of reagent grade or higher purity. The Stoddard solvent (mineral spirits) serving as a solvent for various OMPs reportedly was of commercial grade. Tributyltin methacrylate (TBTM) used for conditioning chromatographic columns was of commercial grade originally, but had been stored at -15 °C for one year before use, with probable degradation. This sample was dissolved in THF without purification.

2.1.2 Instrumental Methods

The SEC-UV/ΔRI-GFAA including a high pressure pump, has been described [4]. The eluent consisted of THF. In some of the experiments, discrete quantities of THF (50 μL or 500 μL) containing 1.0 percent acetic acid (v:v) were injected at measured intervals after injection of solutions of the polymer dissolved in the THF [6].

GFAA measurements were taken both on-line [7] and off-line. For off-line measurements, discrete volumes (0.5 to 1.0 mL) of effluent were collected in vials during a chromatographic run for subsequent tin quantitation. Individual specimens were diluted with appropriate, measured volumes of THF to assure that GFAA readings were taken within the scale of linear response.

Tin recovery was calculated by comparing the amount of signal, summed over all of the discrete, collected volumes, with that of a sample injected into the sample loop and collected before entering the SEC column.

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*Certain suppliers of chemicals and equipment are identified by name in order to specify the experimental conditions adequately. This does not imply endorsement or recommendation by the National Bureau of Standards nor does it imply that the particular brands of chemicals and equipment named are necessarily the best for the purpose.

Except for one experiment, the SEC columns consisted of µStyragel
(Waters Associates, Milford, MA) having a nominal average pore size of
10^2 Å, 10^3 Å, or 10^4 Å. Columns of these different pore sizes were used
in several combinations.

Several experiments were performed to test the hypothesis that a
dissociation mechanism results from exposure of the tributyltin-bearing
polymer to aromatic groups in the solid phase. These experiments
included using one, two, or three columns in series, following their
regeneration by treatment with acetic acid as described above; and two
sets of three columns pretreated individually with a solution of either
OMP or of TBTM in THF. Tables and figures summarizing experimental
results also outline the individual experimental conditions.

For molecular weight (MW) estimation, columns were calibrated with
a series of standard samples of polystyrene in THF (Arro Labs,
Joliet, IL) [4].

2.1.3   Treatment of Data

The determination of number and weight average MW by GFAA has been
described in detail [4]. In the present work we used a manual
procedure [8] for calculating MW from SEC-ΔRI chromatograms. This
consisted simply of tracing a peak onto graph paper and then cutting
out, at 1/2 cm intervals, and weighing strips of paper subtending the
SEC peak. The MW assigned to each strip was estimated at its center for
the present experiments. For low MW species, usually present in much
smaller amounts, the MWs were estimated from their elution volumes,
determined at the intersection point of lines tangent to the sides of
the peak. Number and weight average MW values were calculated from the
same formulae (equations 1 and 2) for both SEC-GFAA and SEC/ΔRI.

$$M_w = \frac{\Sigma h_i m_i}{\Sigma h_i} \tag{1}$$

$$M_n = \frac{\Sigma h_i}{\Sigma h_i / m_i} \tag{2}$$

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Each h_i represents either the height of a GFAA peak or the weight of a
0.5 cm segment of the peak cut out along its base (ΔRI).

The extent of polymer conversion was calculated from equation 3:

$$\Delta P(\%) = \frac{(P)}{(P + M)} \times 100 \qquad\qquad (3)$$

where ΔP is the degree of conversion, P is a parameter depending on
polymer content, and M is a parameter depending on the content of
monomer or low MW species. In each case, it is assumed that the areas
represent actual weight fractions of high or low MW species in the
unfractionated mixture.

2.2 NMR

2.2.1   Instrumentation

Instruments used were Bruker Instruments Inc. superconducting NMR
spectrometers operated in the pulse FT mode at field strengths of
4.7 T and 9.4 T. The respective NMR frequencies for H-1, Sn-119, and C-13 are
200, 74.60, 50.31; and 400, 149.20, and 100.62 MHz. Conditions used for
spectral acquisition always included quadrature phase detection and,
when Sn-119 or C-13 spectra were run, broad-band proton decoupling with
normal NOE for C-13, but with NOE suppressed for Sn-119. Primary
chemical shift references used were internal TMS for protons, external
TMS (concentric tube) for C-13, and internal tetramethyl tin for Sn-119;
each of these was assigned a value of 0 ppm. Most of the non-proton
spectra were indirectly referenced to the above standards using the
internal deuterium lock frequency as a secondary reference. All proton
and carbon spectra were run at 9.4 T; tin spectra were run at both 4.7
and 9.4 T. Some spectra run earlier at other field strengths are
included for comparison. Normally a pi/2 pulse was used. Table 1 gives
typical operational NMR parameters for the nuclei investigated.

Table 1. Typical NMR Parameters

Nucleus	Frequency MHz	Sample size mg/ml	Tube diam mm	Spectral Range[a] ppm	No. of points[b]	Hz/point	No. of scans
H-1	400.13	5/.5	5	-.5 to 4.5	8K	.488	64
C-13	100.62	500/3	10	-10 to 60	16K	.854	10000
				160 to 200	16K	.488	10000
Sn-119	74.6	4000/15	20	-20 to 129	8K	2.714	5000

[a]Both sweep offset and sweep width are adjusted to achieve the desired
 spectral range.

[b]1K = 1024

2.2.2   Cleavage of Tributyltin from OMP

Tin-free polymer was prepared for proton and C-13 NMR spectral
examination as follows: Solvent is removed from polymer by
evaporation, and 5 g of dried polymer is dissolved in 20 mL of
chloroform. To this solution is added 2 mL of 12 N HCl and the mixture
is shaken. A precipitate of poly (MMA-MAA) appears. The tributyltin
groups remain in solution as tributyltin chloride. The precipitate is
separated from the supernatant by decantion and is then dried. The dried
tin-free polymer is dissolved in pyridine (4 mL pyridine per g of
solid). Proton and C-13 NMR signals from pyridine occur in regions of
the spectrum where there are no polymer signals, so that the pyridine does
not interfere with spectral interpretation.

3.0 Results and Discussion
3.1 SEC
3.1.1   Evidence Supporting a Cleavage Mechanism

Earlier SEC-GFAA results from this laboratory showed a distribution
of tin in OMPs in a high MW fraction, a low MW fraction, and a cationic

species that is absorbed on µStyragel [4,9,10]. The latter species is readily desorbed by trace quantities of acetic acid in THF, with nearly quantitative tin recovery [6]. Chromatograms of an OMP fractionated on an acid pretreated column, however, show very little tin associated with the high polymer fraction, but large proportions of tin-bearing adsorbed species (table 2, fig. 1).

Table 2.   Summary of SEC-GFAA[a] for OMP-2N

	Polymer (%)[b]	Monomer (%)[b]	Adsorbed Species (%)[b]	Recovery (%)[c]
	7.54	0.94	91.5	79.7
	5.39	0.86	93.7	80.3
	4.36	0.22	95.4	88.2
	8.03	0.66	91.3	61.5
	4.31	0.52	95.2	69.2
	4.48	0.48	95.0	72.8
X	5.69	0.61	93.7	75.3
s	1.68	0.26	1.9	9.4
n = 6		6	6	6

[a]Column: µStyragel 10^3 Å, one.
[b]Percent of total tin observed.
[c]Percent of total tin injected.

Nevertheless, the same OMP shows a much larger proportion of polymer in the ΔRI chromatogram and Sn-119 NMR spectra failed to detect the loss of large quantities of tin from the polymer prior to injection (fig. 2; see detailed analysis in subsection 3.2.5). This indicates on-column dissociation of the tin-bearing moieties from the polymer chain. We suggest a mechanism involving complexation of tin-bearing cationic species formed by dissociation with

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SEC-ΔRI GFAA CHROMATOGRAMS OF OMP-2N

ON μSTYRAGEL (10^3 Å) WITH DESORPTION

OF TIN-BEARING CATIONS BY DILUTE ACETIC ACID

Desorbed species

ΔRI

Polymer

ΔRI

Monomer

GFAA (TIN)

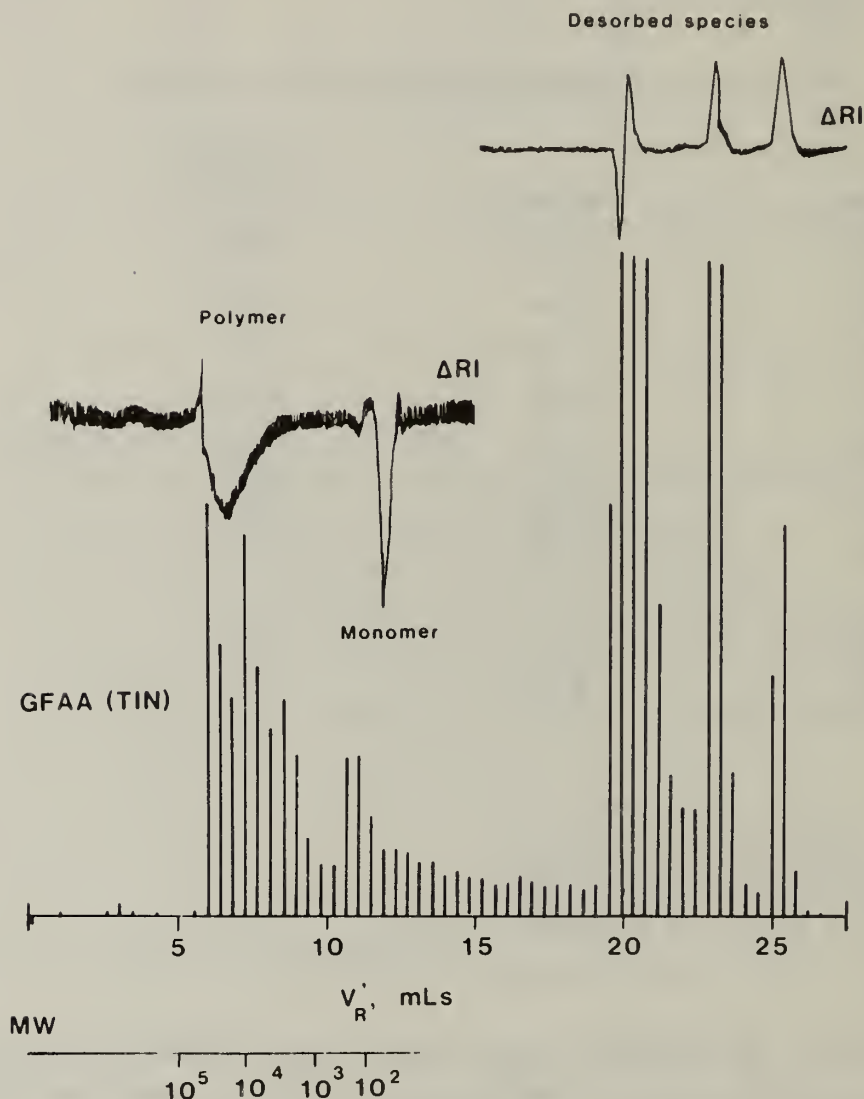5   10   15   20   25

V_R', mLs

MW

10^5 10^4 10^3 10^2

Figure 1. SEC-ΔRI-GFAA chromatograms of OMP-2N.   Solvent, THF.   Column, μStyragel (one), average pore size 10^3 Å.   Mobile phase, THF. Flow rate, 0.5 mL min⁻¹.   Detector Perkin-Elmer 360 equipped with Sn-specific EDL lamp operating at 224.6 nm.   Injected sample volume 50 μL; concentration 0.38 mg/50 μL.   HOAc in THF (1.0 % v/v) injected (50 μL) 18 min after polymer, and at 5 min intervals thereafter, ΔRI sensitivity, 1 X 10 ⁶ ΔRI for full scale deflection, decreased to 5 X 10 ⁶ ΔRI at 15 mL.
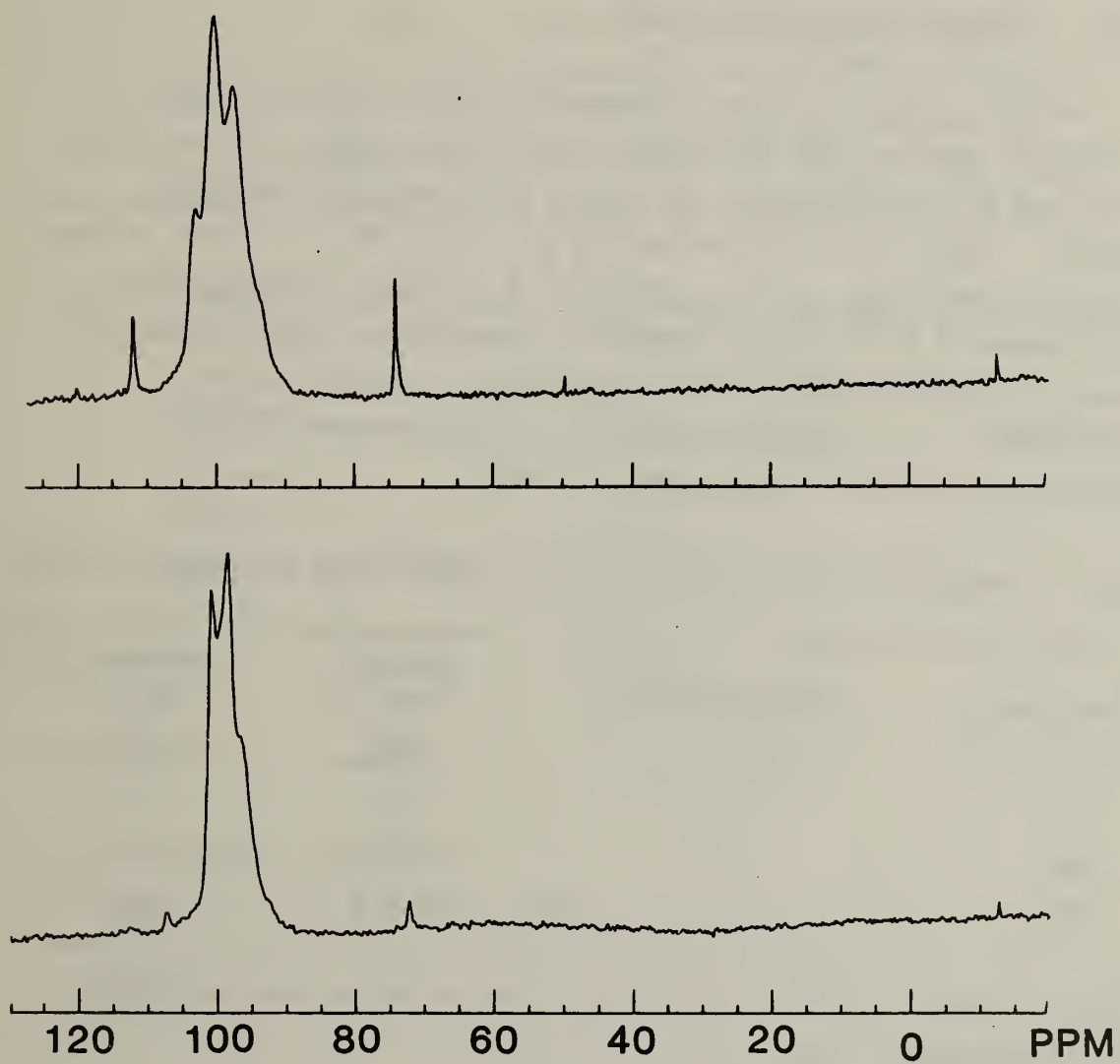
Figure 2. Tin-119 at 74.6 MHz of OMPs in chloroform. (A) OMP-2P;
          (B) OMP-8P.

aromatic groups incorporated in the polymer chains of which the packing material is comprised. In view of our earlier successful experiments in the SEC-GFAA of OMPs [4,9] the current data indicate that column conditioning is critical and involves either equilibration of cationic species with the packing surface or chemical deactivation. A set of experiments was devised to test this hypothesis.

3.1.2 Demonstration of Cleavage

3.1.2.1 Varying Length of Column

The data (table 3) clearly demonstrate that the dissociation of tin-bearing species from the polymer chain occurs mainly on the first column and is not affected by the number of subsequent individual columns. A 500 µL solution containing 6.5 mg of OMP in THF was injected into either one, two, or three 30-cm 10^3 Å µStyragel columns, using a mobile phase of THF, and ΔRI detection. The polymer fraction and the monomer fraction were collected consecutively for off-line tin determination. The adsorbed species were then desorbed with a 1.0 percent solution of acetic acid in THF.

Table 3. Analytical SEC of OMP-2P[a] with column length (µStyragel) varied.

Column Length (cm)[b]	Polymer Fraction (%)[c]	Monomer Fraction (%)[c]	Adsorbed for Species (%)
30	7.7	18.1	74.1
60	9.9	2.5	87.7
90	7.9	2.0	90.1

[a]500 µL injected solution containing 6.8 mg of unfractionated polymer.
[b]10^3 Å µStyragel, 7.8 mm i.d.
[c]Fraction of total tin recovered.

Less than 10 percent of the total observed tin is associated with the polymer fraction eluted from either one, two, or three columns (table 3); less than 3.0 percent is associated with the low MW species

eluted from two or three columns, and a large preponderance of tin-bearing species is adsorbed on the column packing.

3.1.2.2   Varying Sample Size

Injecting relatively large amounts of OMP partially conditions the SEC packing, reducing the extent of cleavage as an injected sample of OMP traverses the column. When 50 µL of the same polymer solution, containing 0.65 mg of OMP, was injected on three columns in tandem, less than 3.0 percent of the eluted tin was associated with the eluted polymer, and less than 1.0 percent with the eluted low MW species; 95 percent of the adsorbed tin-bearing species is found on the first column and about 5 percent on the second and third columns (table 4).

Table 4.   Analytical SEC of OMP-2P on 90 cm of µStyragel (3 columns): Distribution of Adsorbed Tin Species

Fraction	Location	Percent[a]
Polymer	Eluted	2.69
Monomer	Eluted	0.67
Adsorbed Species[b]	Col. #1	95.1
" "	Col. #2	0.78
" "	Col. #3	0.77

Tin Recovery[c]:   67.0 percent

[a]Percent of total tin observed.

[b]Desorbed with aid of 1.0% HOAc in THF.

[c]Percent of total tin injected with 50 µL of solution containing 0.68 mg of polymer.

We infer that a small number of tin-to-polymer bonds (less than three percent) are exceptionally stable, and that large quantities of sample promote deactivation of the solid phase. A test of this hypothesis will include preparatory scale fractionation of an OMP on surface-active SEC packing, separation of the polymer fraction, and examination of this

fraction by FT-NMR for tin-to-carbon rather than tin-to-oxygen bonds. A set of commercial OMPs (0.65 mg per injected specimen) all manifested similar, small proportions of polymer tin, when elution of adsorbed species was forced by means of repeated injections of 50 μL volumes of 1.0 percent acetic acid in THF. These data verify the hypothesis that column conditioning or deactivation by appropriate cationic species is necessary for successful SEC-GFAA of OMPs. Desorption of such species by dilute acetic acid in THF regenerates surface activity that cleaves tin-bearing cations from long-chain OMPs.

3.1.2.3 Methylene Chloride As Mobile Phase

To determine whether THF might act as a solvating agent, thereby promoting dissociation of the tin-polymer bond, methylene chloride was substituted for THF as mobile phase. The result was a single peak eluted from a single column after 11 mL of eluent (fig. 3A). Substituting THF as eluent resulted in the appearance of another peak appearing 11 mL after introduction of THF onto the column (1st peak in fig. 3B). But a solution of OMP in methylene chloride, injected into a mobile phase of THF, gave polymer and monomer peaks with elution volumes identical to those obtained with OMP dissolved in THF (2nd and 3rd peaks in fig. 3B). Thus it is evident that methylene chloride, although a good solvent, is not a satisfactory chromatographic eluent for OMPs.

3.1.2.4 Propyl Modified Silica As Solid Phase

This packing material provided a polymer peak and a very long tail (fig. 4) without evidence of a low molecular weight peak. Since this tailing indicates a serious absorption problem, no additional experiments were undertaken using these columns.

3.1.2.5 Deactivation of μStyragel

3.1.2.5.1 Prior Overloading with OMP

Three selected 10^3 Å μStyragel were conditioned individually by injecting 5.0 mg of an OMP in 500 μL of THF. Although used extensively for analysis of oil specimens, these columns had not been previously exposed to acetic acid. A plate count showed them to be individually and in tandem, in good condition, with 20,000 theoretical plates per meter.

A sample of OMP fractionated on these columns gave the SEC-ΔRI and the SEC-GFAA chromatograms shown in figure 5, indicating that: (1) the

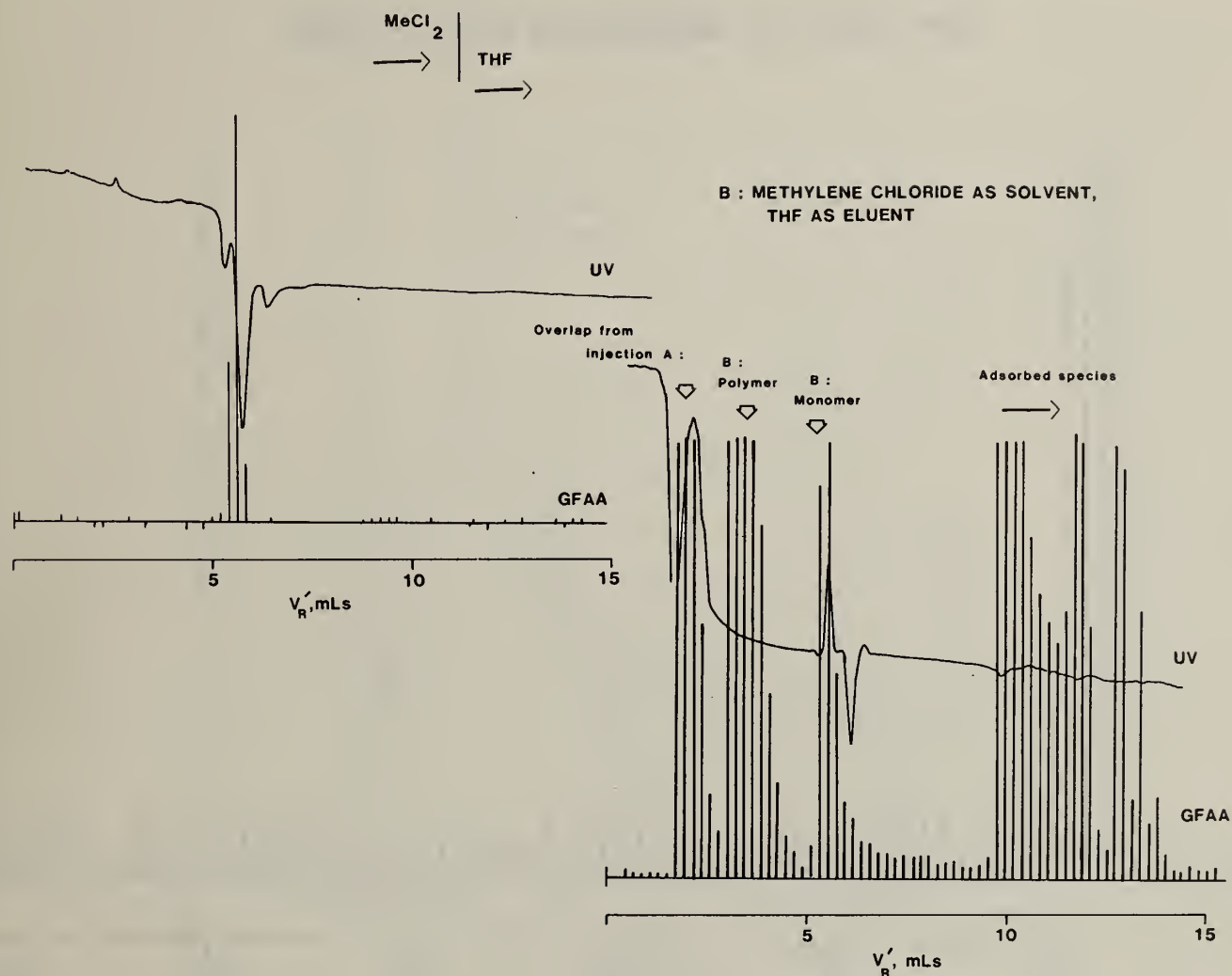A : METHYLENE CHLORIDE AS SOLVENT AND
      ELUENT FOR OMP-2P

MeCl₂
——→ THF
        ——→

B : METHYLENE CHLORIDE AS SOLVENT,
      THF AS ELUENT

UV

Overlap from
injection A :
                B :
                Polymer   B :
                             Monomer   Adsorbed species
                                                    ——→

GFAA

5   10   15

V_R',mLs

UV

GFAA

5   10   15

V_R', mLs

Figure 3. SEC-GFAA of OMP-2P. (A) solvent, methylene chloride. Mobile
         phase CH_2CL_2 for the first 25 mL, then THF. Flow rate 0.5 mL
         min [1]. Injected sample 0.45 mg/50 μL. UV sensitivity 0.0125
         AUFS. Column the same as for figure 1. (B) Solvent CH_2Cl_2,
         eluent THF. Other conditions as above. Acetic acid injected
         16 min after the polymer solution and at 2 to 5 min intervals
         thereafter.

SEC-GFAA CHROMATOGRAM OF OMP-2P
ON PROPYL-MODIFIED SILICA GEL
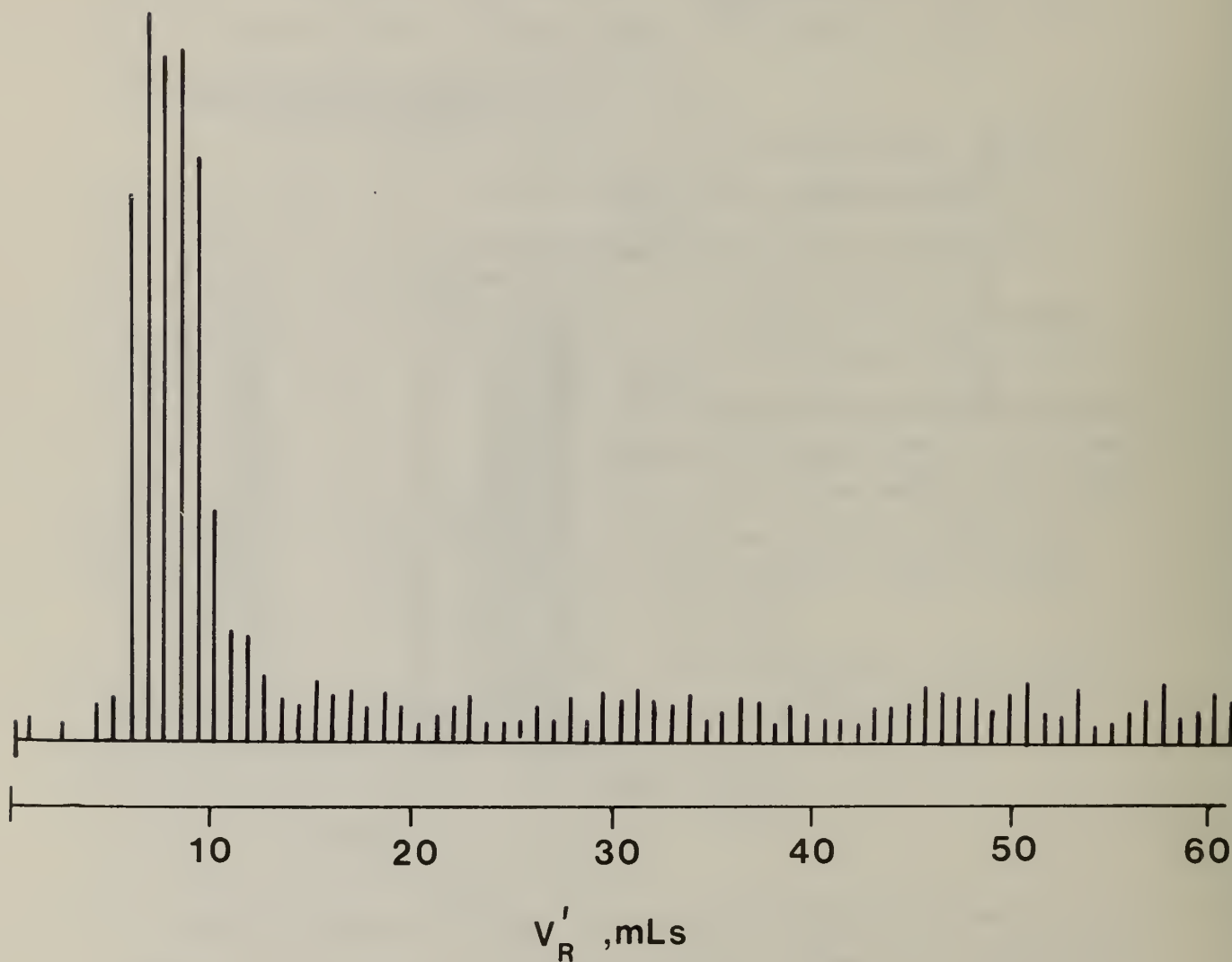

V_R' ,mLs

Figure 4. SEC-GFAA of OMP-2N. Columns, propyl substituted silica gel (two). Average pore size 10^2 and 5×10^2 Å; dimensions 4.6 mm i.d. X 250 mm. Other conditions the same as for figure 1, omitting acetic acid.
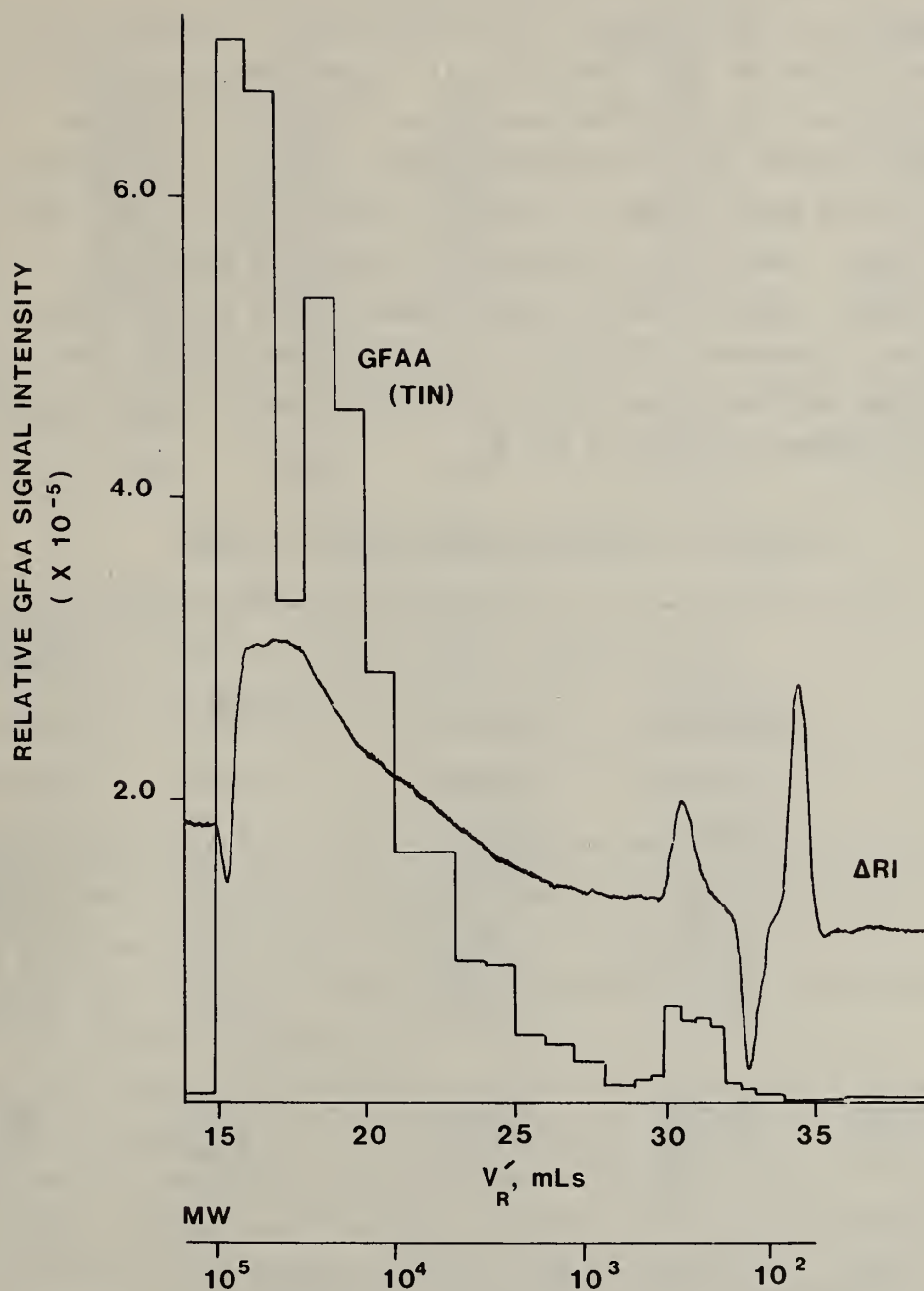
Figure 5. SEC-ΔRI, GFAA chromatograms of OMP-2N. Columns μstyragel
(three), pore size 10^3 Å. Solvent, THF. Eluent THF. Flow
rate 1.0 mL. min^{-1}. Injected sample volume 5.0 mg/500 μL.
0.5 mL fractions collected for off-line GFAA. ΔRI sensitivity
1×10^{-6} ΔRI unit per full scale deflection.

triorganotin species indeed is bonded to polymer, and (2) that it remains so when eluted through a deactivated column.

Asymmetry in the SEC/ΔRI high polymer peaks indicates total exclusion of part of this fraction. It is necessary to use SEC columns of greater pore size for MW determinations. Figure 6 includes SEC-UV/ΔRI, SEC-UV, SEC-GFAA chromatograms of OMP-2P, a commercial polymer, using three columns in tandem of pore size 10^4, 10^3, and 10^2 Å, respectively. The column calibration is indicated below the chromatograms. Each column was deactivated with a 500 µL injection containing 2.0 percent of tributyltin methacrylate (TBTM). The data for this polymer and four other preparations dissolved in mineral spirits are all presented in tables 5 and 6.

Table 5. SEC-ΔRI Chromatography of OMPs[a]

Sample Number	M_w (daltons)	M_n (daltons)	MWD	Mass Conversion (%)
OMP-8N	46,000	31,300	1.49	96.7
OMP-8P	50,000	28,400	1.75	96.3
OMP-2N	52,300	32,600	1.56	96.2
OMP-2P	63,700	40,900	1.56	96.6
"	69,700	36,900	1.88	95.7
"	62,800	33,900	1.85	95.8
OMP-2P				
Average	65,400	37,200	1.76	96.0
S. D.	3,750	3,500	0.18	0.5
n	3	3	3	3

[a]Columns (µStyragel) 10^4 Å, 10^3 Å, 10^2 Å, in series.
[b]Conversion of low to high-MW species.

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Table 6. SEC, GFAA Chromatography of OMPs[a]

Sample Number	M_w (daltons)	M_n (daltons)	MWD	Conversion[b] (%)	Recovery[c] (%)
OMP-8N	35,300	13,900	2.53	89.9	104.0
OMP-8P	37,800	15,000	2.52	95.9	93.4
OMP-2N	41,600	18,500	2.25	90.0	94.1
OMP-2P	65,000	28,500	2.28	92.5	111.0
"	56,900	24,900	2.29	92.1	97.3
OMP-2P					
Average	61,600	26,700	2.28	92.3	104.2
S. D.	5,700	2,500	0.01	0.3	9.7
n	2	2	2	2	2

[a] Columns (µStyragel) 10^4 Å, 10^3 Å, 10^2 Å.
[b] Conversion of low MW tin-bearing species to polymer.
[c] Ratio of eluted to injected tin.

There appears to be little difference between the samples prepared by DTNSRDC (OMP-2N and OMP-8N, figs. 8 and 9) and the corresponding commercial formulations (OMP-2P and OMP-8P, figs. 6 and 7). It is also apparent in tables 5 and 6 that the MW determinations are reproducible within plus or minus 10 percent.

The fact that a UV peak nearly coincides with both the ΔRI and the GFAA peaks strongly indicates that chromophoric species are bonded to the tin-bearing low molecular weight species having a MW of about 650 to 1000 daltons. The molecular weight suggests a compound or complex of tributyltin (or a degradation product) with a chromophoric organic acid such as benzoic acid, or methacrylic acid.

The explanation suggested is consistent with NMR spectra (fig. 10). The NMR peak at 101.5 ppm in figure 10 may be due to tributyltin benzoate. A sample of tributyltin benzoate run by itself in chloroform has the identical chemical shift. Note however that complexation with benzoic acid is possible only for OMP-N polymers, since OMP-P polymers are made with an aliphatic peroxide as initiator rather than benzoyl
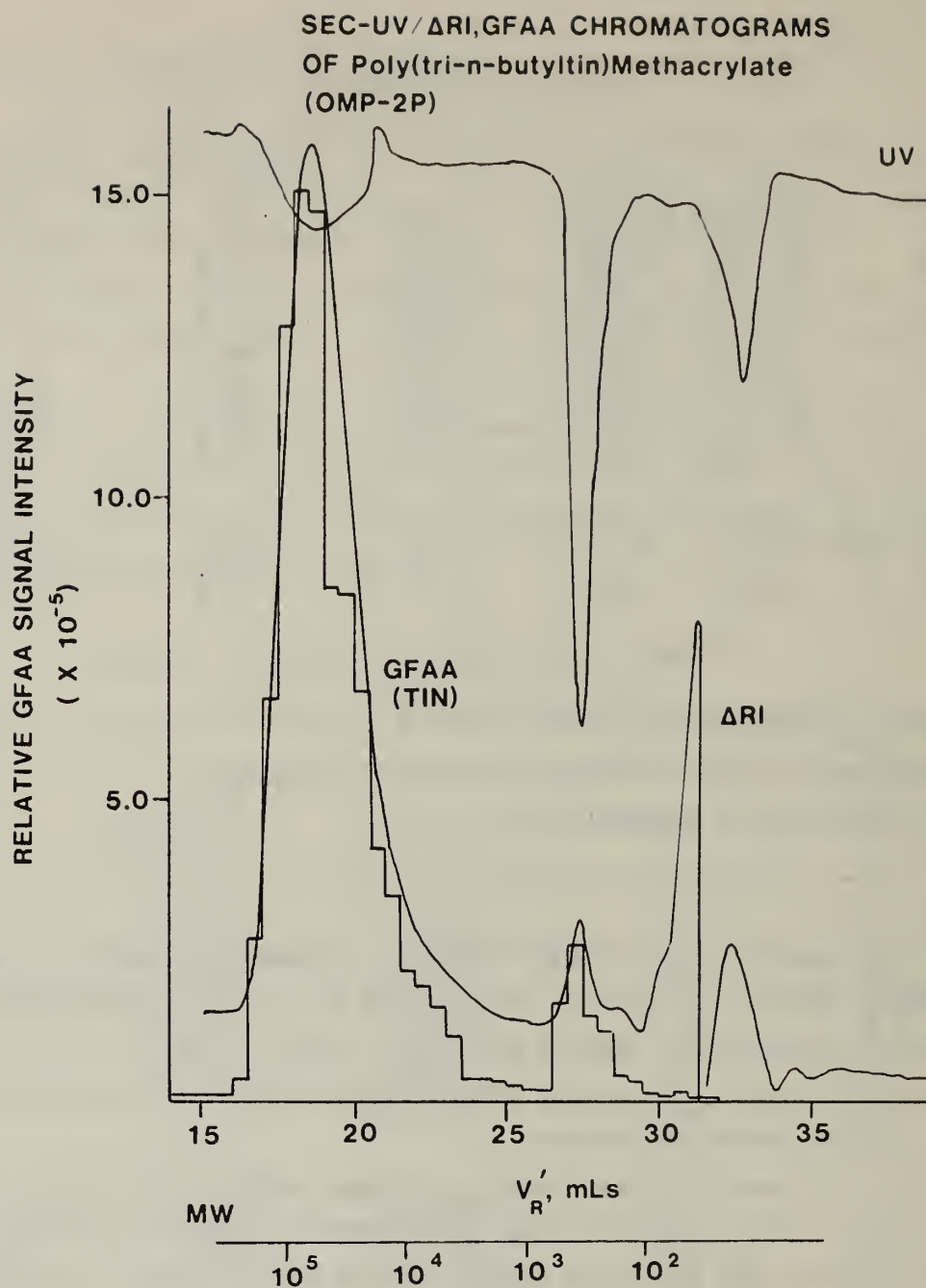
Figure 6. SEC-UV/ΔRI, GFAA chromatograms of OMP-2P. Columns, μStyragel (three), pore size 10^4, 10^3, and 10^2 Å, consecutively. Solvent THF. Eluent THF. Flow rate 0.5 mL min^{-1}. Injected sample 4.2 mg/500 μL. 0.5 mL fractions collected for off-line GFAA. UV sensitivity 0.1 AUFS. ΔRI sensitivity 1 X 10^{-6} ΔRI unit for full scale deflection.

SEC-UV/ΔRI,GFAA
CHROMATOGRAMS
OF OMP-8P

ΔRI

UV

RELATIVE GFAA SIGNAL INTENSITY
(X 10^{-5})

GFAA
(TIN)

10.0

5.0

20   25   30   35

V_R',mLs

MW

10^5 10^4 10^3 10^2
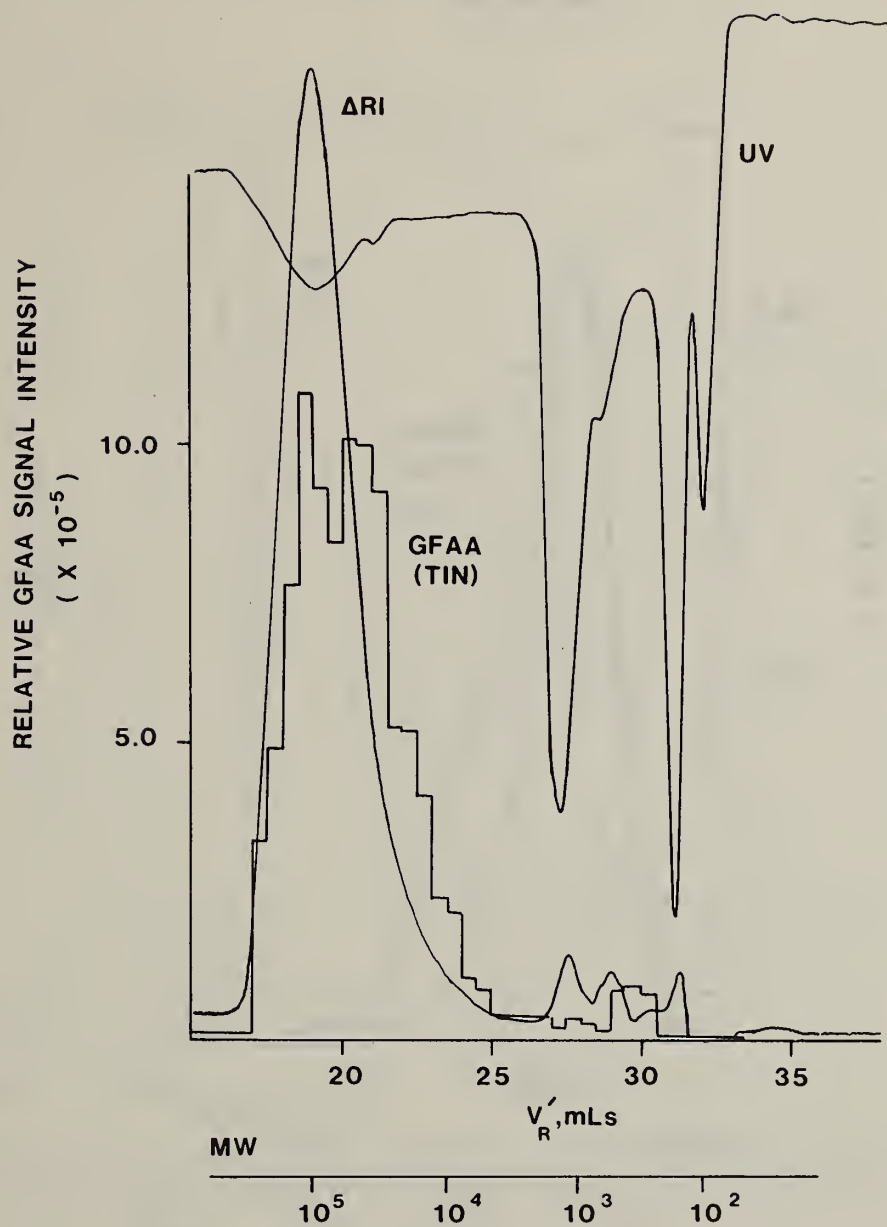
Figure 7. OMP-8P. All conditions the same as figure 6. Injected sample,
4.9 mg/500 µL.

SEC-UV/ΔRI,GFAA CHROMATOGRAMS
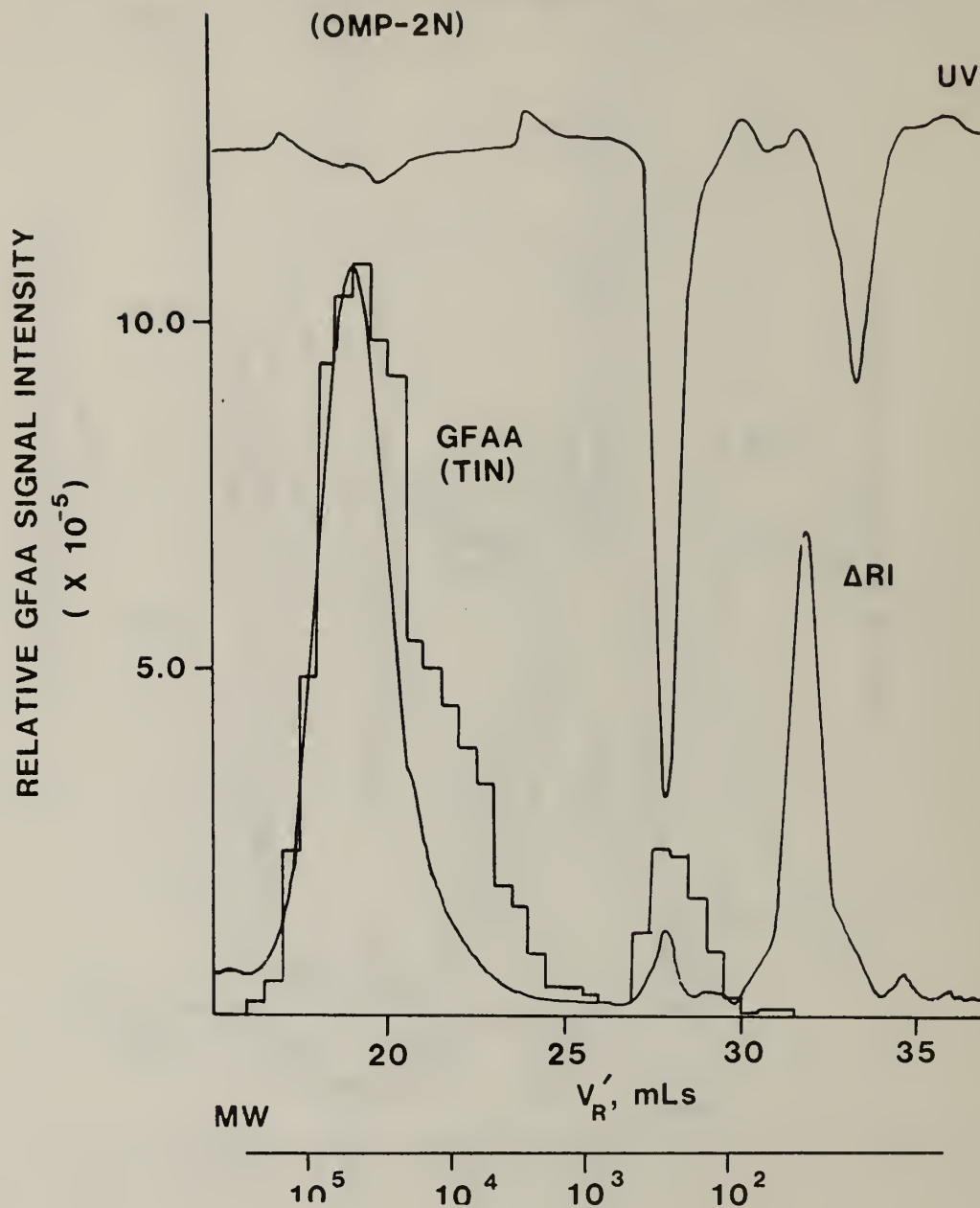OF Poly(tri-n-butyltin)Methacrylate
(OMP-2N)

Figure 8. Sample OMP-2N. All conditions the same as figure 6. Injected
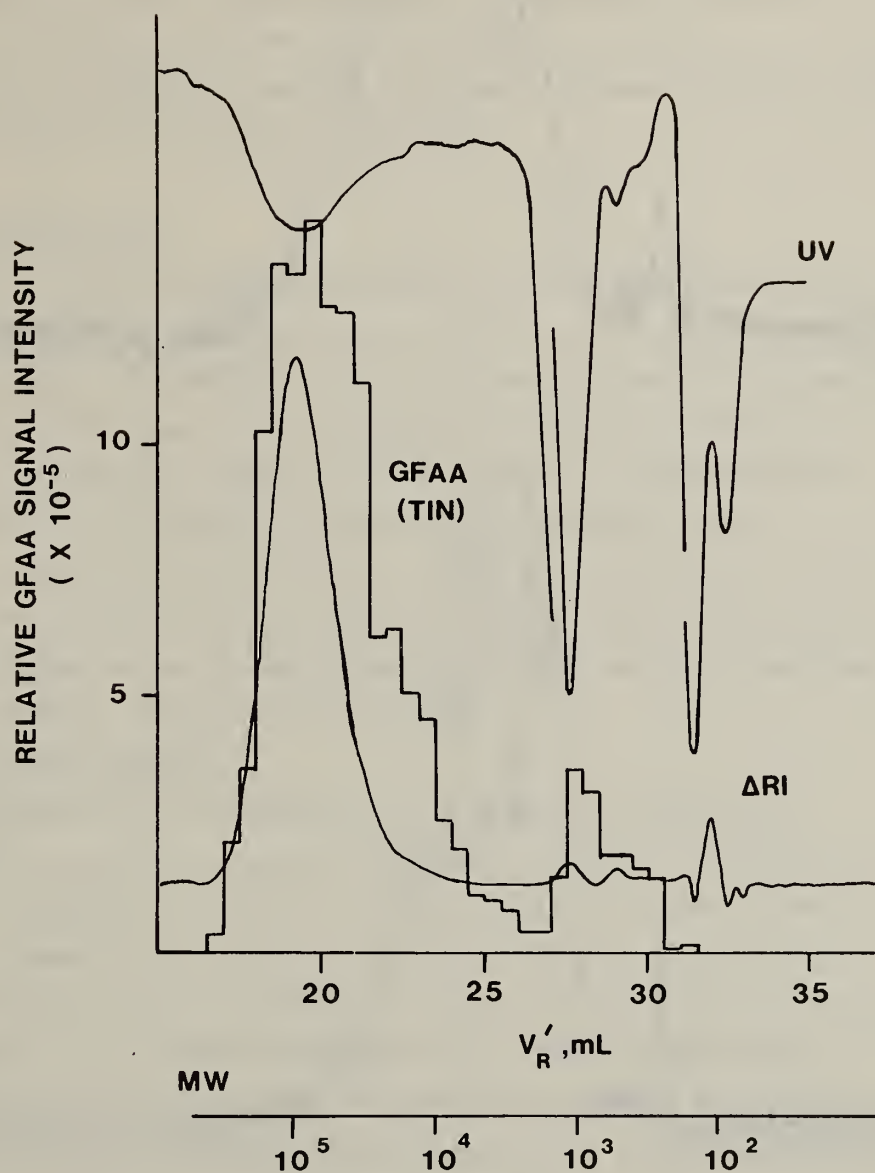sample, 4.6 mg/500 μL.

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SEC-UV/ΔRI ,GFAA
CHROMATOGRAMS
OF OMP-8N

Figure 9. OMP-8N. All conditions the same as figure 6. Injected sample, 5.8 mg/500 μL.
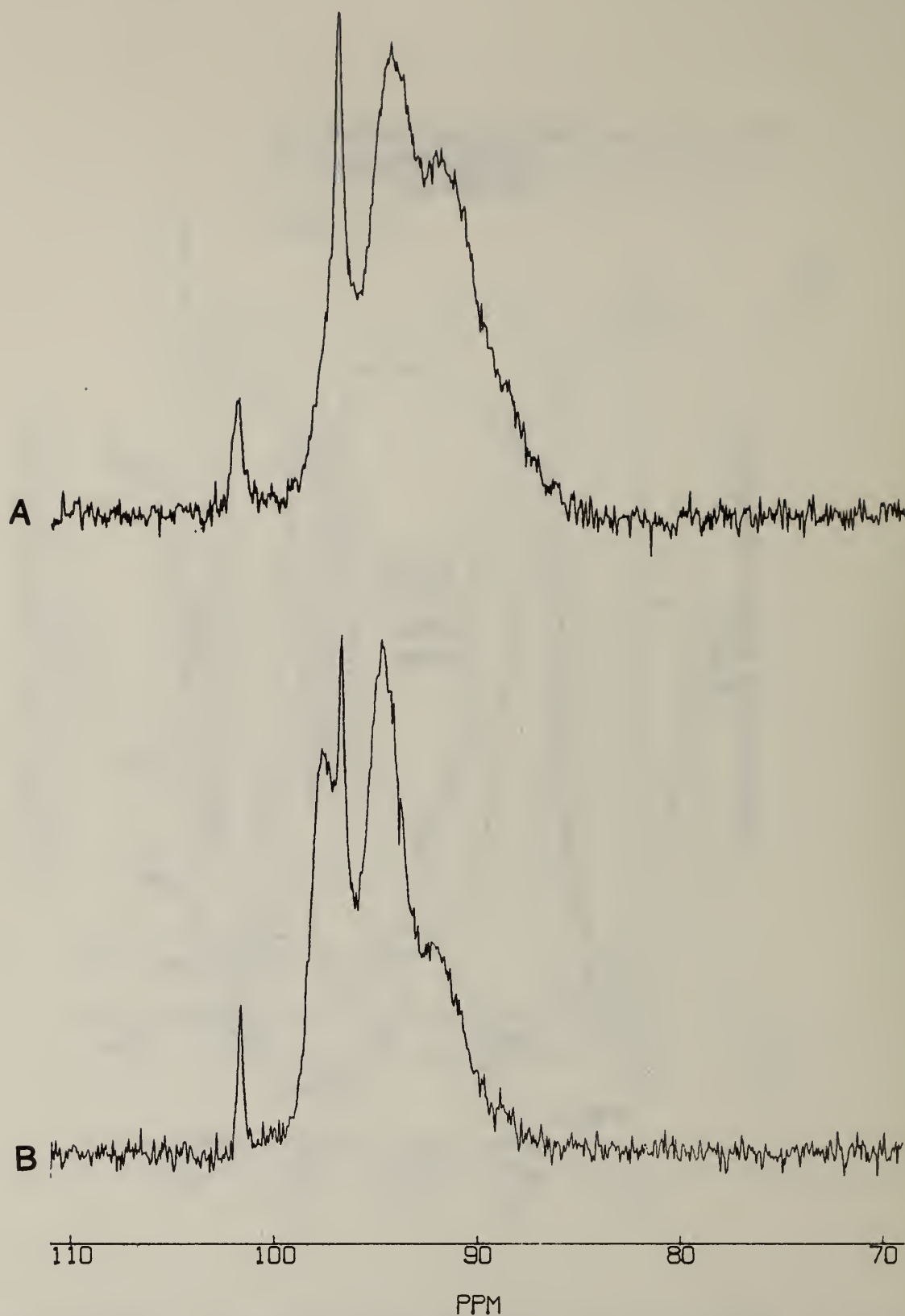
21

Figure 10.   Tin-119 NMR at 74.6 MHz of OMPs in benzene.   (A) OMP-2N;
              (B) OMP-8N.   In each spectrum the sharp peak at about 97 ppm
              arises from unreacted TBTM.

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peroxide. An NMR peak at about 97 ppm in OMP-P polymers is attributed later in this report (subsection 3.2.5) to tributyltin methacrylate (see fig. 25). However, further work needs to be performed on the identification of the low MW chromophore--e.g., collection of fractions during preparatory scale chromatography for subsequent analysis by ultraviolet, infrared, and NMR spectroscopy.

Appendix A presents in detail a suggested method for SEC-UV/ΔRI, GFAA characterization of OMPs on μStyragel.

3.2 NMR

3.2.1 Introduction

Since the last report [6] was published, we have succeeded in the complete configurational sequencing, at the triad level, of copolymers of MMA and TBTM or MMA and MAA. The copolymerization of vinyl monomers of A and B can give rise to triad sequences which are syndio-(rr), hetero-(mr), or iso-(mm) tactic. At the same time, compositional sequences such as AAA, AAB, BAB, ABA, BBA, and BBB may occur. Hereinafter, we will use A to refer to MMA, and B to refer to TBTM or MAA. With both composition and tacticity taken into account, there are 20 possible triad sequences which may exist [5]. We have examined NMR spectra of protons, carbon-13, and tin-119.

3.2.2 Solvent Effects

The polymers that we received for examination contained approximately 33 percent solids, dissolved in either a commercial mixed hydrocarbon (Stoddard) solvent or in an aliphatic ketone solvent. The NMR spectra, especially of tin, showed such large differences in appearance between these two solvents that a study of solvent effects was undertaken. It is well known that tin, which is nominally 4-coordinate in these polymers, can readily expand its coordination shell to five or six, and that donor solvents may promote such expansion [11]. In the absence of coordinating solvents, it appears likely that tin will expand its coordination number by self-association with ester groups in other parts of the polymer.

The results of a study of solvent effects in OMP-2 solutions are given in figure 11. It is clear that for best resolution, chloroform is the preferred solvent. In subsequent Sn-119 NMR experiments, polymer solution was diluted with an equal volume of $CDCl_3$, and the spectrometer
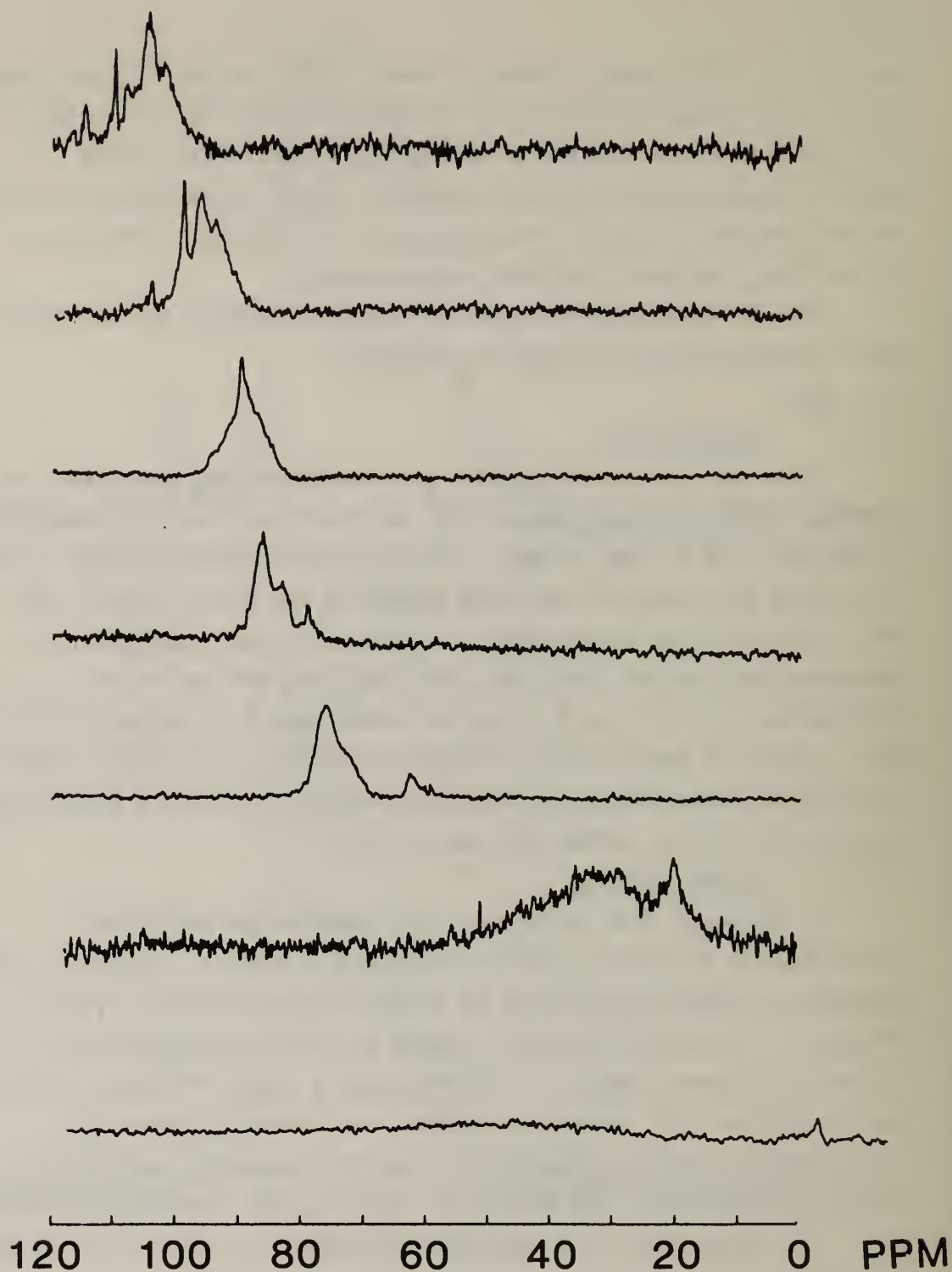
23

Figure 11.   Tin-119 NMR at 74.6 MHz of OMP-2P in several solvents.
From the top: chloroform, benzene, n-hexane, acetone,
tetrahydrofuran, methanol, and pyridine.

was locked to the deuterium signal. This not only improved field stability for long accumulations, but also provided a frequency reference so that the signal could be referenced to external tetramethyl tin. In the discussion that follows, the shape and relative positions of various tin signals are of considerable significance. However, because of the large solvent effects and the uncertainties associated with external referencing, absolute chemical shift values have little meaning (in these concentrated solutions, the polymer must be regarded as both solute and a part of the solvent system).

3.2.3 Protons

Proton spectroscopy has been valuable for characterizing the tin-free polymers (MMA-MAA). These include not only the prepolymers but also material obtained by cleavage of tributyltin groups from OMPs (see above). In these polymers, proton NMR of the $-CH_2-$ units in the polymer backbone gives an unequivocal determination of tacticity [12]. The $-CH_2-$ signal, occurring about 1.8 ppm, is diagnostic for dyad sequences (r or m). In the syndiotactic groups (r), the signal is a single peak at the chemical shift position. In isotactic groupings (m), however, the protons are magnetically inequivalent and hence appear as a doublet approximately equally spaced (by about 0.35 ppm) on either side of the syndiotactic peak. Because of the inequivalence, each line of the doublet is split into two by the geminal H-H coupling of about 14 Hz, so that altogether 4 lines are seen. Integrals of the singlet and the quartet allow the tacticity to be determined quantitatively. Tetrad splittings (rrr, rrr, rrm,...) have not been observed in these samples. A sample of poly (MMA) was prepared by butyllithium-induced polymerization of MMA at -78 °C [13] and was shown by H-1 NMR to be predominantly isotactic (m) [14]. Figure 12 shows the 400 MHz proton NMR of isotactic DMMA prepared as described above. The pair of doublets at 1.55 and 2.20 ppm are diagnostic of the isotactic $-CH_2-$ group. The small peak at 1.8 ppm in the expanded spectrum represents the residual syndiotactic groups. The narrow $\beta-CH_3$ signals at 1.2 ppm(mm), 1.0 ppm(mr), and 0.85 ppm(rr) give an indication of triad frequencies (86.4 : 8.4 : 3.1). These figures are incompatible with Bernoullian statistics, in agreement with previous reports on anionic polymerization of MMA [16]. Having only dyad and triad frequencies, we are unable to test any Markov model.
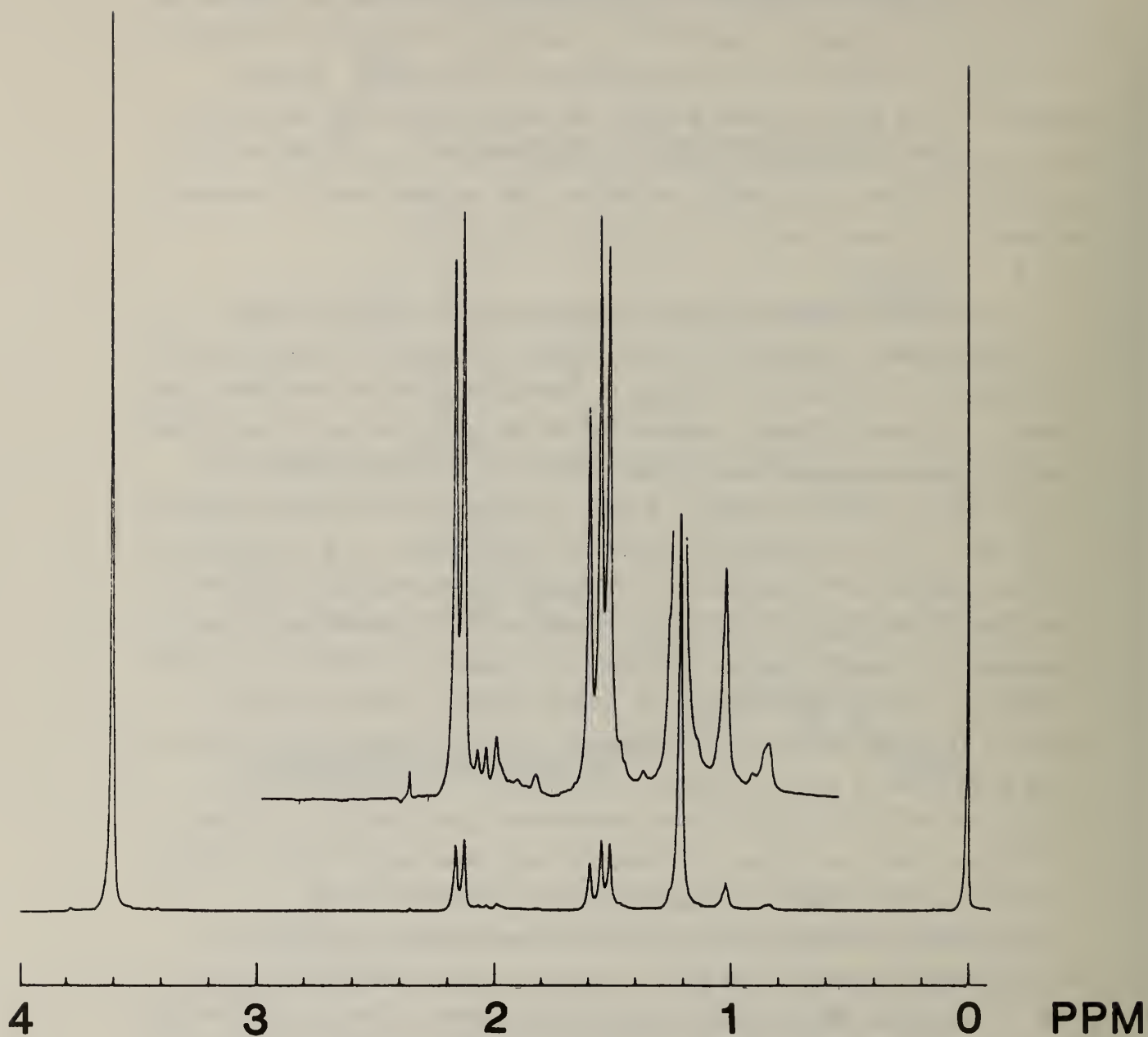
Figure 12.   Proton NMR at 400 MHz of isotactic PMMA dissolved in CDCl$_3$. Upper trace 8X vertical expansion.

Figure 13 shows the 400 MHz proton NMR of a commercial 1:1 prepolymer (MMA-MAA). The -CH_2- signals at 1.7 to 1.9 ppm arise from -CH_2- groups between COOR, COOR; COOH, COOR; and COOH, COOH. All of these groupings are seen to be syndiotactic since the regions at 1.55 and 2.20 ppm are free from signal. The β-CH_3 region is expected to show two signals, each split by compositional sequencing as well as tacticity effects. The complexity of the signals seen indicates that compositional effects are large; the lines have not been assigned. In tin-containing polymers, the protons of the butyl groups give strong signals which make the signals from the rest of the polymer difficult or impossible to observe and proton NMR is consequently less useful. Figure 14 shows the 400 MHz proton NMR of OMP-2P. The butyl groups are responsible for nearly all of the strong signal to high field of 1.7 ppm. The β-methyl group is completely obscured. However, the signal at 1.8 ppm together with the absence of signal at 2.20 ppm shows that the polymer is also predominantly syndiotactic.

3.2.4   Carbon-13

The least sensitive nucleus in these compounds, carbon-13, is also the most informative. The chemical shift range covered in the C-13 spectrum of the polymer runs from about 10 to 185 ppm (if a ketonic solvent is present, its carbonyl absorption will occur at about 205 ppm) (see fig. 15). The final copolymers show such large interferences in the aliphatic region from the butyl groups (and solvent in the samples as-received) that only the carbonyl region (around 180 ppm) is useful. In order to get more exact structural information, we have removed the tributyltin groups from the polymer by treatment with HCl and extraction with chloroform, as described above. In the copolymer of MMA and MAA thus prepared, which is directly comparable with the commercially prepared pre-polymer, it is possible to distinguish much configurational information. In the C-13 spectrum of the pre-polymer (see fig. 16 and 17), the NMR signals fall into five distinct regions and are informative to varying degrees. In order of increasing chemical shift, these are β-methyl (15 to 21 ppm), quaternary carbon (44 to 45 ppm), methoxyl (50 ppm), methylene (50 to 55 ppm), and carbonyl (177 to 181 ppm).

Comparison of samples derived from OMP-8 (1:1 vs 2:1 ratio of MMA to TBTM or MAA) enabled us to distinguish, in the carbonyl region, a
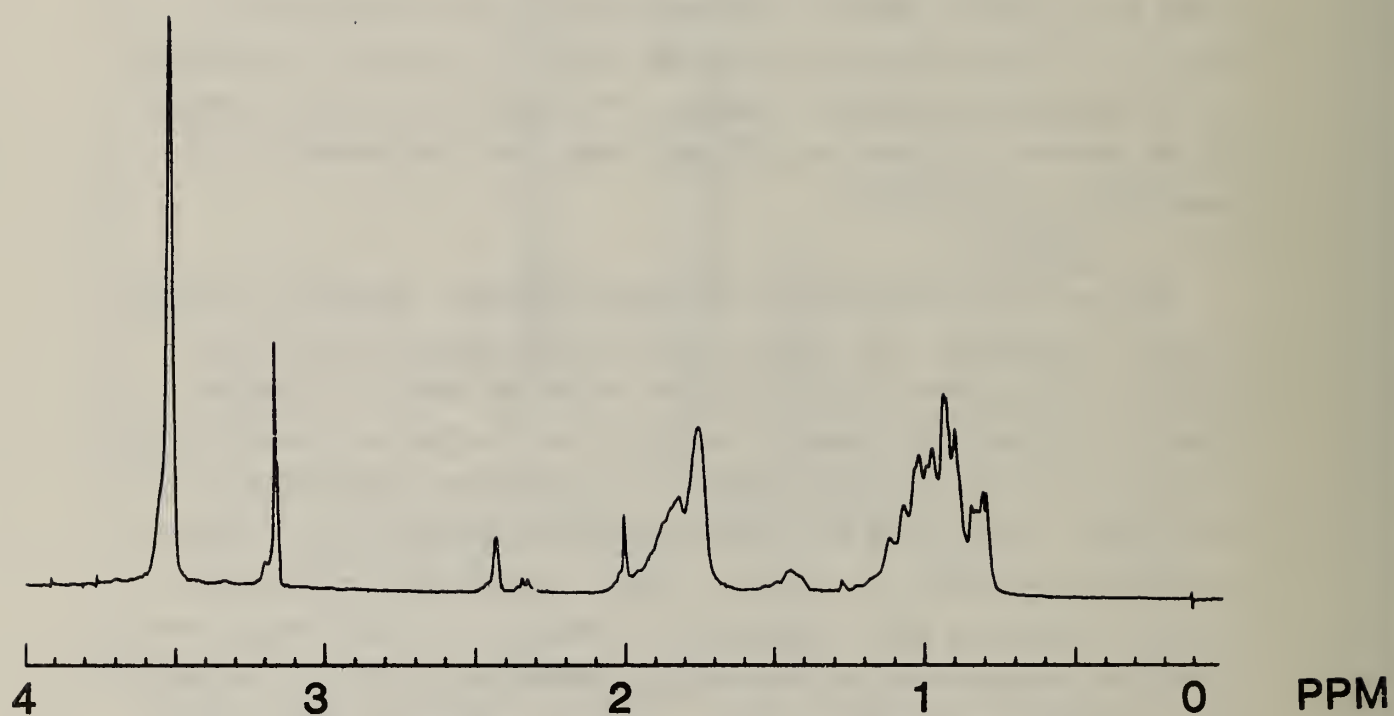
27

Figure 13.   Proton NMR at 400 MHz of OMP-2P prepolymer in DMSO-d$_6$.
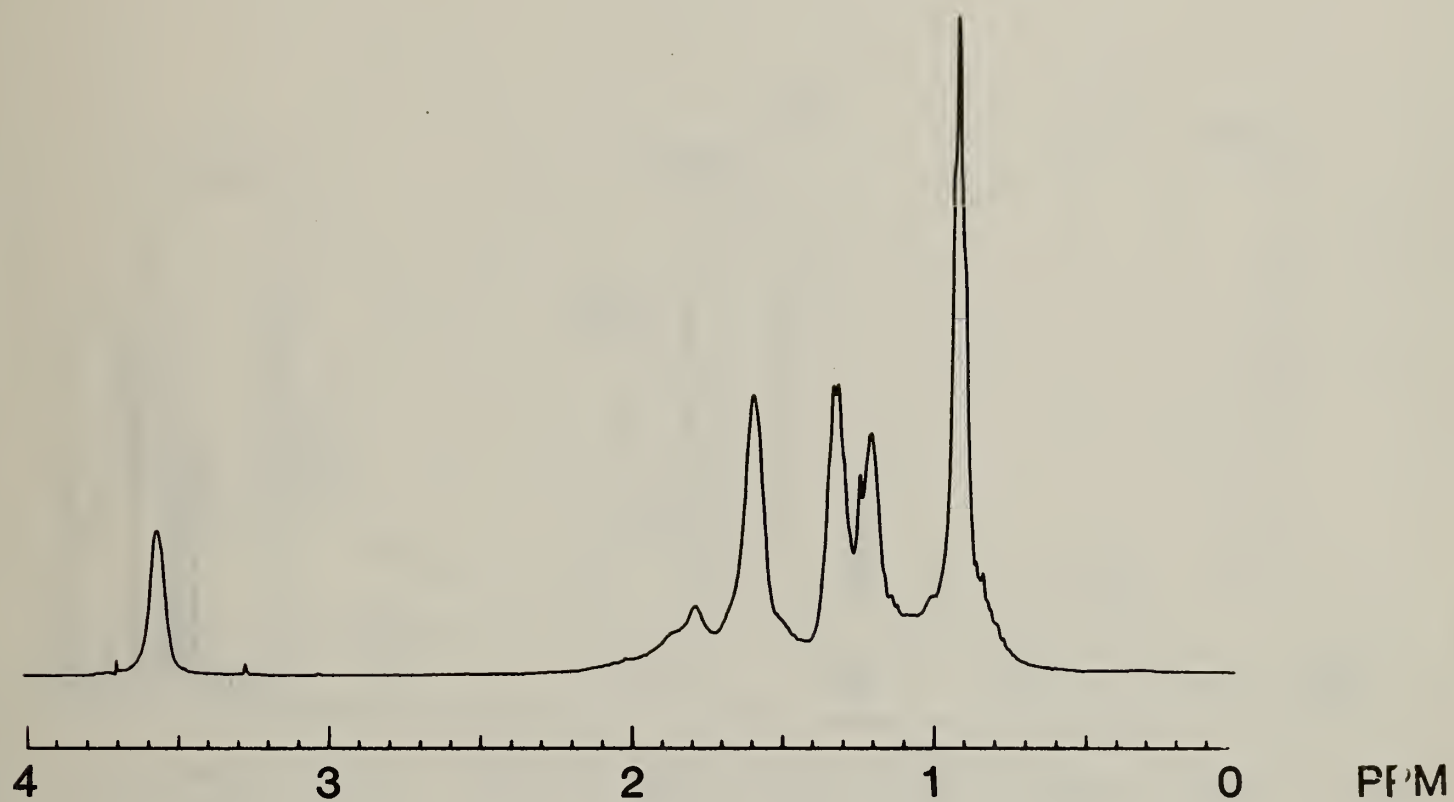
28

Figure 14. Proton NMR at 400 MHz of OMP-2P in CDCl$_3$.
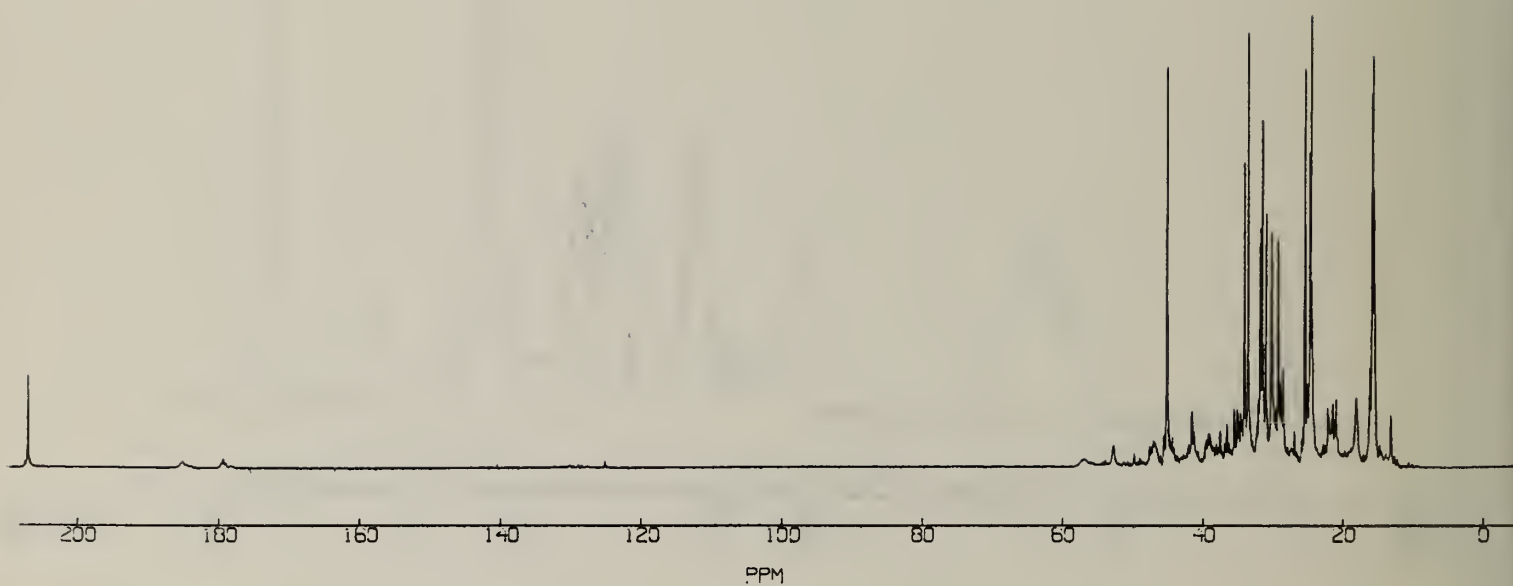
Figure 15.   Carbon-13 NMR at 50.31 MHz of OMP-2P in methyl isoamyl
              ketone, as received.   Most of the signal is due to the solvent.
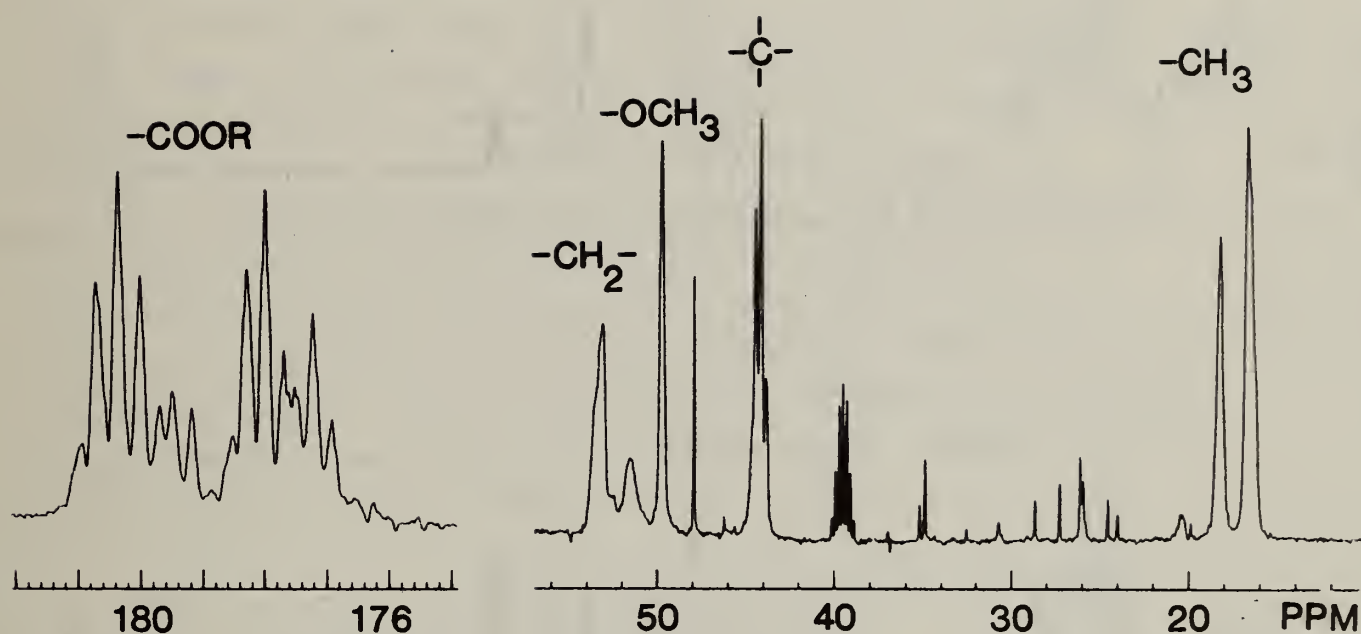
Figure 16.   Carbon-13 NMR at 100.62 MHz of OMP-2P prepolymer in
              pyridine. The major signals are labelled. The weak
              signal at 39.5 ppm comes from DMSO-d_6 in a concentric
              tube. The weak signals between 21 to 35 and at 48 ppm
              are not positively assigned; they may be due to small
              amounts of the original solvent which was not completely
              removed. They are in the wrong position to arise from
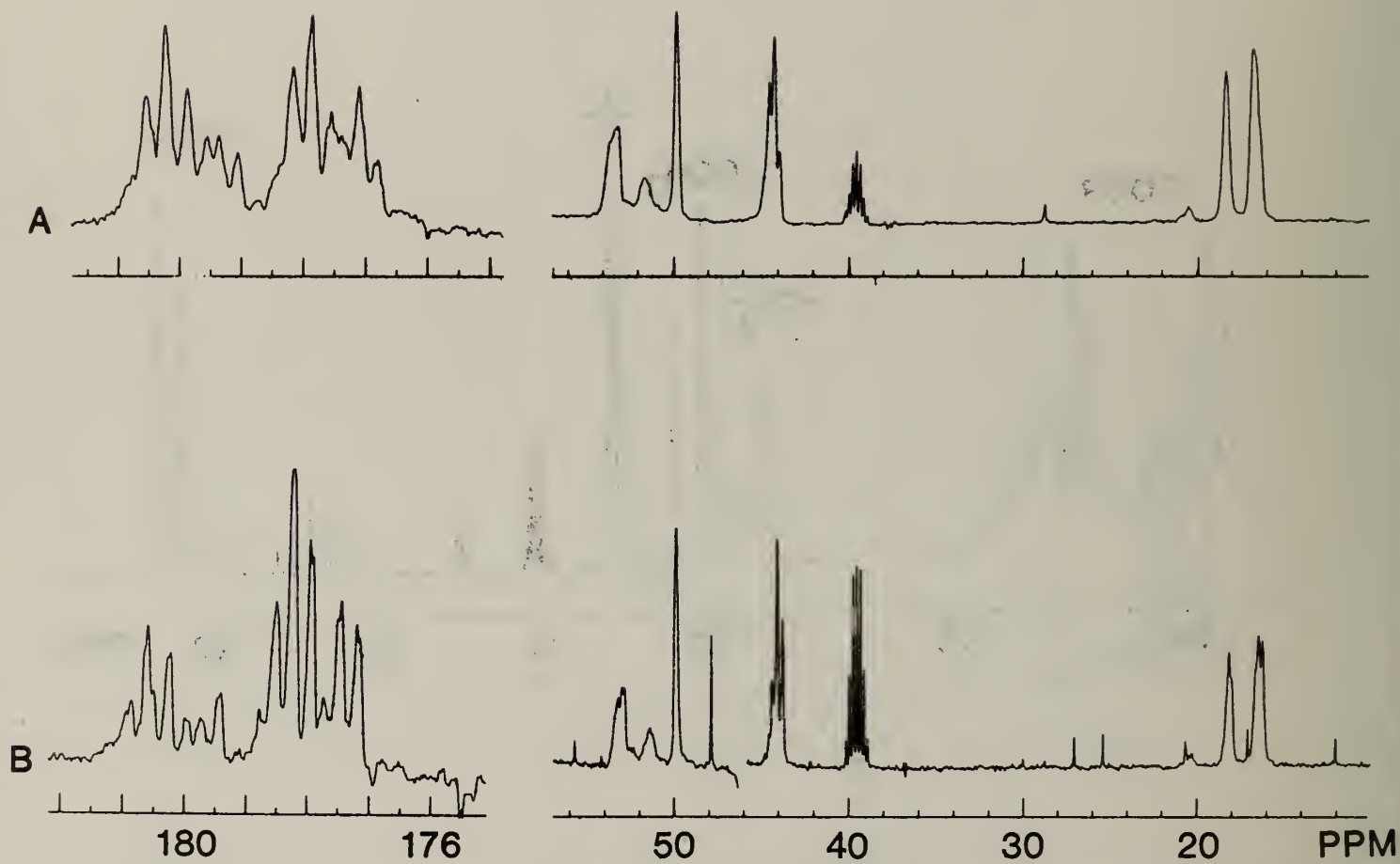   residual tributyltin groups.

Figure 17.   Carbon-13 NMR at 100.62 MHz of polymer stripped of tin
by treatment with chloroform and HCl, and dissolved in
pyridine at 360 °K.   (A) OMP-2N; (B) OMP-8N.

correspondence between structure and chemical shift, in the sense that
-COOMe signals appear at higher field than -COOH or -COOSnR$_3$ signals.
Beyond that, we were able to determine from the relative intensity of
signals in the various multiplets, which of the multiplets were split by
compositional sequencing effects (quaternary carbon), which by tacticity
(β-methyl), and which by both (carbonyl). The methoxyl signal, although
sharp, is but a single line in all samples studied and conveys no
sequencing information. The methylene carbon signal is split into two
broad peaks (r and m) which reflect dyad tacticity, but with poor
precision as the signals are weak. For the three groups to be discussed
below, tacticity effects appear in triads (rr, rm, or mm) and pentads
(rrrr...mmmm). The β-methyl region of the spectrum (15 to 21 ppm) is
relatively unaffected by compositional sequencing but is split into
three well-resolved peaks according to tacticity (fig. 18). The
material is known from proton NMR to be predominantly syndiotactic, and
the largest peak was thus assigned to the (rr) configuration. The
proportions of the three peaks agree with Bernoullian statistics, as
expected for a free-radical catalyzed polymer [15]. Table 7 lists the
proportions of iso-, hetero-and syndio-tactic configurations for several
polymers derived from analysis of the β-Me spectrum. The OMP-2N samples
were run after cleaving the tributyltin groups.

Table 7. Tacticity and Composition Ratios Taken From ^{13}C FTNMR
          Spectra of Poly (MMA-MAA) Copolymers

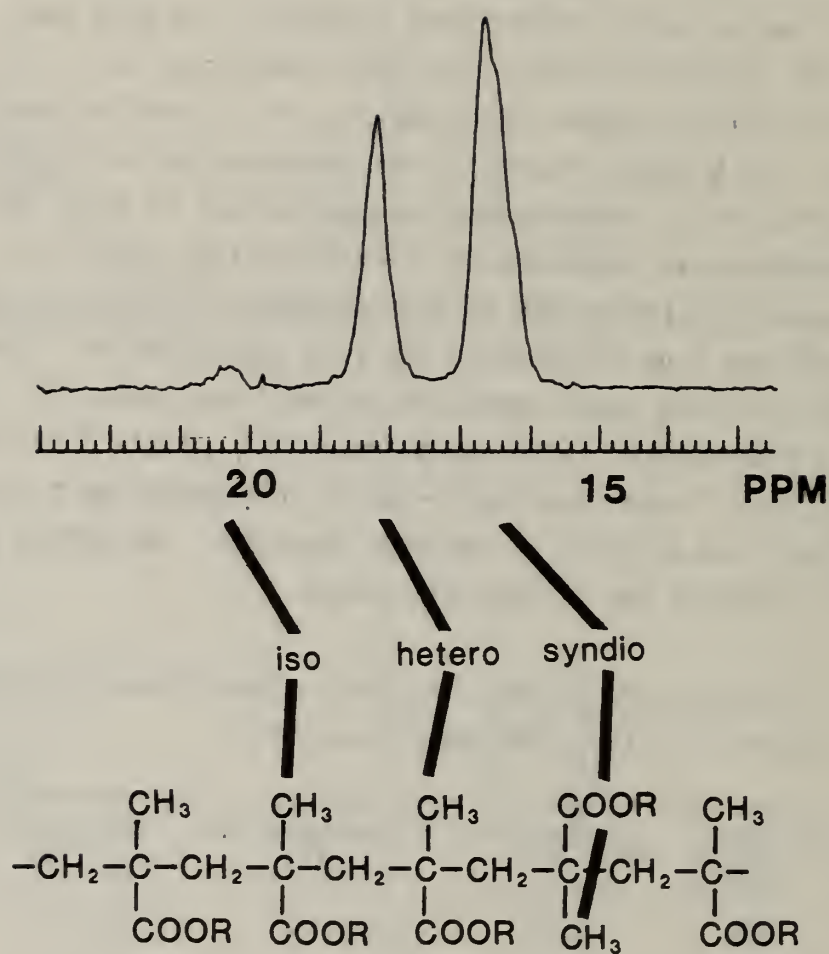| Copolymer Designation	$\dfrac{COOCH_3}{COOH}$	Isotactic (%)	Heterotactic (%)	Syndiotactic (%)
p-TBTM	---	3.0	32	65
OMP-2N	1.0	4.0	37	59
OMP-8N	2.0	5.0	37	58
OMP-2P	0.9	2.0	35	63
OMP-8P	2.4	2.0	40	58

Figure 18.   Carbon-13 NMR at 100.62 MHz of OMP-2P prepolymer in
              pyridine at 360 °K. Expansion of β-Me region. Labelled
              according to tacticity.

correspondence between structure and chemical shift, in the sense that -COOMe signals appear at higher field than -COOH or -COOSnR$_3$ signals. Beyond that, we were able to determine from the relative intensity of signals in the various multiplets, which of the multiplets were split by compositional sequencing effects (quaternary carbon), which by tacticity (β-methyl), and which by both (carbonyl). The methoxyl signal, although sharp, is but a single line in all samples studied and conveys no sequencing information. The methylene carbon signal is split into two broad peaks (r and m) which reflect dyad tacticity, but with poor precision as the signals are weak. For the three groups to be discussed below, tacticity effects appear in triads (rr, rm, or mm) and pentads (rrrr...mmmm). The β-methyl region of the spectrum (15 to 21 ppm) is relatively unaffected by compositional sequencing but is split into three well-resolved peaks according to tacticity (fig. 18). The material is known from proton NMR to be predominantly syndiotactic, and the largest peak was thus assigned to the (rr) configuration. The proportions of the three peaks agree with Bernoullian statistics, as expected for a free-radical catalyzed polymer [15]. Table 7 lists the proportions of iso-, hetero-and syndio-tactic configurations for several polymers derived from analysis of the β-Me spectrum. The OMP-2N samples were run after cleaving the tributyltin groups.

Table 7.   Tacticity and Composition Ratios Taken From ^{13}C FTNMR
            Spectra of Poly (MMA-MAA) Copolymers

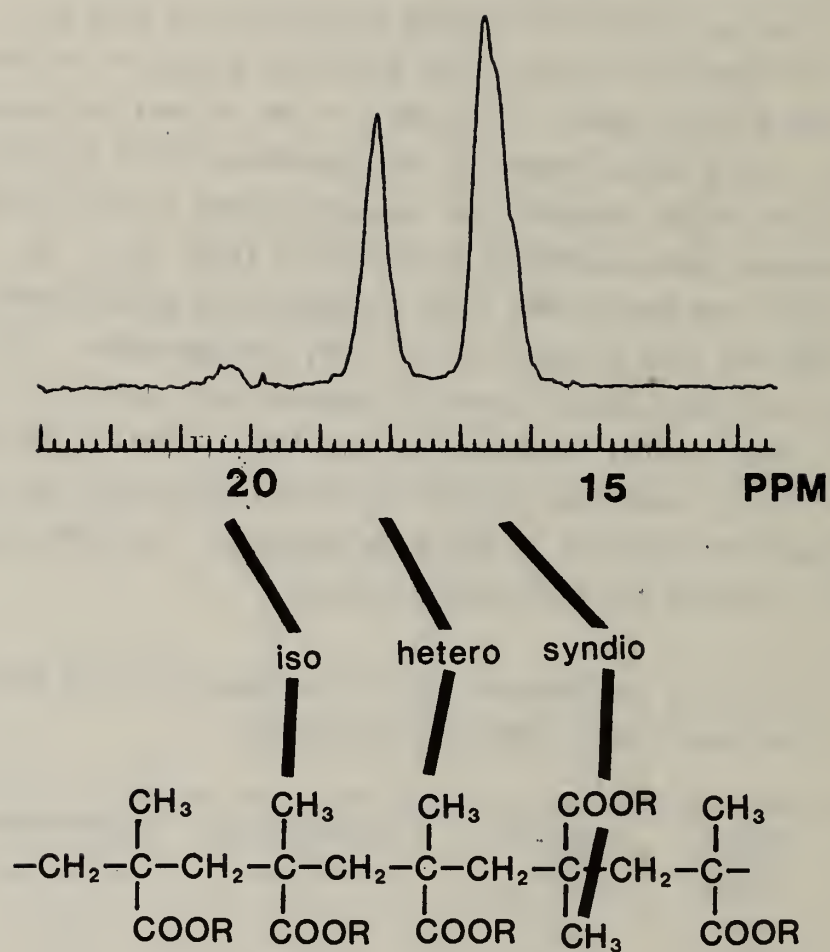| Copolymer Designation	COOCH$_3$ / COOH	Isotactic (%)	Heterotactic (%)	Syndiotactic (%)
p-TBTM	---	3.0	32	65
OMP-2N	1.0	4.0	37	59
OMP-8N	2.0	5.0	37	58
OMP-2P	0.9	2.0	35	63
OMP-8P	2.4	2.0	40	58

Figure 18.   Carbon-13 NMR at 100.62 MHz of OMP-2P prepolymer in pyridine at 360 °K. Expansion of β-Me region. Labelled according to tacticity.

A sample of isotactic PMMA (see above) was about 20 percent hydrolyzed [15] to a poly (MMA-MAA). The C-13 NMR spectrum of thus-prepared isotactic poly (MMA-MAA) allowed the assignment of the isotactic (mm) peaks unequivocally. The quaternary carbon region primarily reflects the effects of composition, and to a lesser degree tacticity. A quaternary carbon bonded to -COOMe shows a relatively sharp line with shoulders rather than discrete splittings to indicate a distinction between AAA, AAB, and BAB. A quaternary carbon bonded to -COOH appears as a broad, structureless peak which is uninformative. Because the broad and sharp peaks overlap, integrals of the quaternary region are of little value. The carbonyl region of the spectrum is split into a great many lines and is consequently informative (figs. 19, 20). The upfield (-COOMe) and downfield (-COOH or -COOSnR$_3$) signals show considerable parallelism. Each may consist of a triplet of triplets. The larger triplet splitting (about 1.2 ppm) is caused by tacticity. In order of increasing field strength (decreasing chemical shift) the peaks arise from syndio(rr), hetero(rm), and iso(mm)-tactic material. In figure 20 the amount of syndio- and heterotactic polymer is too small to be seen. The smaller triplet splitting (about 0.5 ppm) is caused by compositional sequencing effects as diagrammed in figure 20. The additional small splittings in the carbonyl region are probably due to pentad structure; however, they have not been assigned. Knowing that the 2:1 polymer must have a smaller proportion of B groups, we can assign the triplets as follows: downfield--AAA; center--BAA + AAB; upfield--BAB. Correspondingly, the B triplet sequence is ABA, BBA+ABB, BBB in order of increasing field. It is not possible by means of C-13 NMR to determine the amount of residual -COOH in the presence of -COOSnR$_3$, because the chemical shifts of all signals in these species are virtually coincident. Impurity signals are not present in large amounts. If present in small amounts, they would be masked by solvent in the as-received material since the solvent C-13 NMR spectrum is very rich in signals. The tin-free samples have had the solvent and solvent impurities replaced by pyridine.

3.2.5   Tin-119

Tin-119 NMR is useful on two counts: it provides a means of finding and determining tin-containing impurities, and it also provides
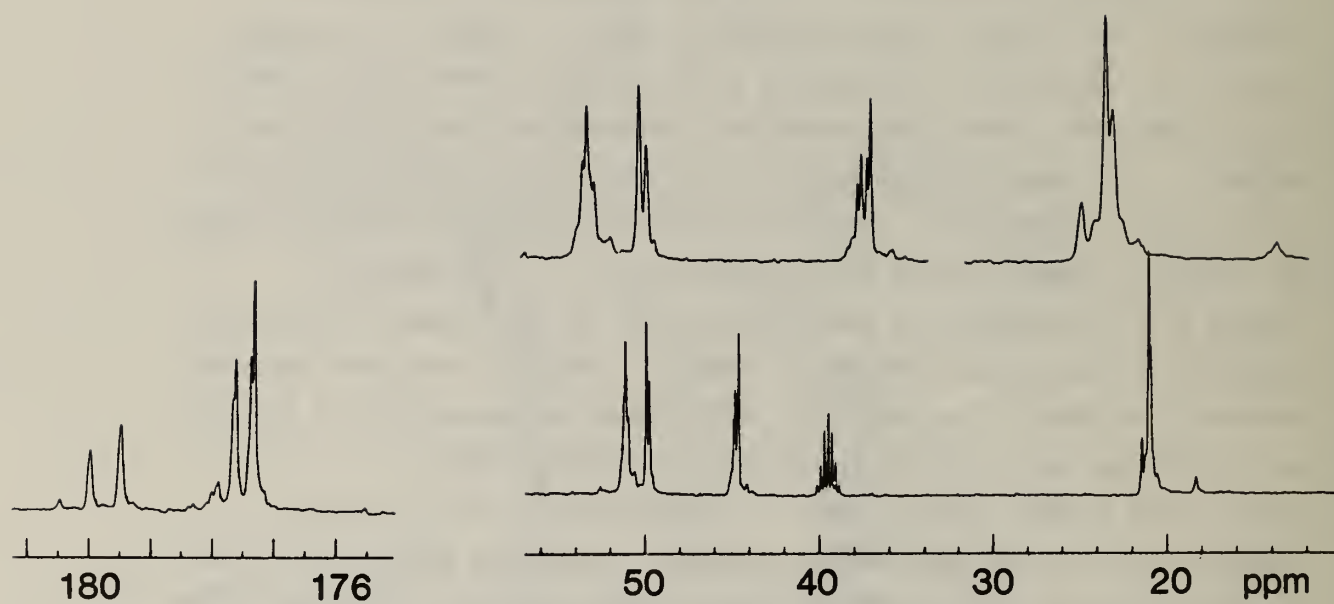
Figure 19.   Carbon-13 NMR at 100.62 MHz of isotactic poly(MMA-MAA) in pyridine at 360 °K. Upper trace 2.5X horizontal expansion.
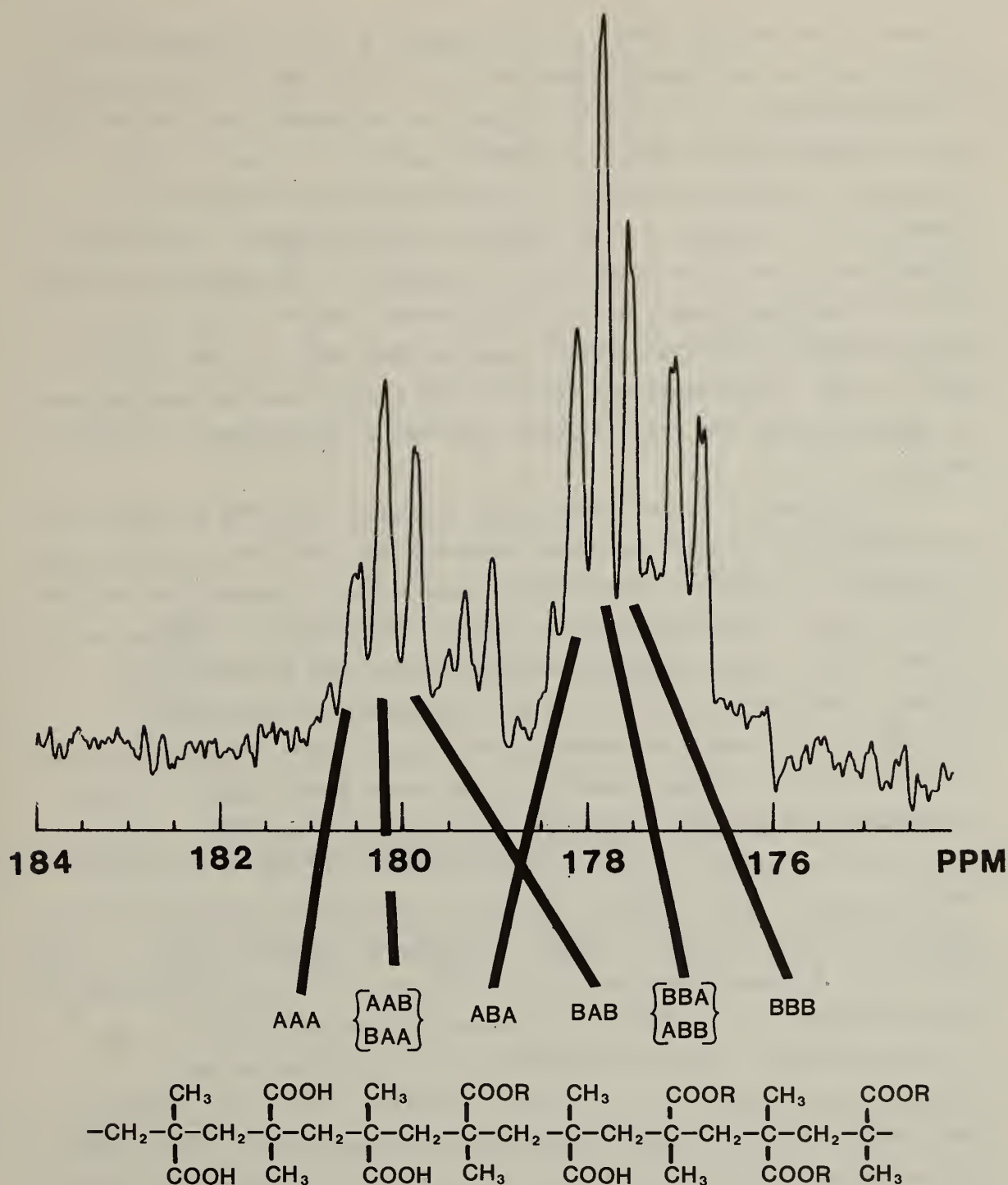
Figure 20.   Carbon-13 NMR at 100.62 MHz of OMP-8P prepolymer in
              pyridine at 360 °K.   The syndiotactic peaks are labelled according
              to composition.   The weak higher field peaks are caused
              by heterotactic polymer; there is too little isotactic
              material to be detected.

a means of estimating compositional sequencing. By using material of which a portion has been stripped of tin for C-13 NMR, it was possible to determine that the Sn-119 NMR signal, which appears as a rather broad peak at about 90 to 98 ppm in chloroform solution, is but little affected by tacticity, whereas it shows structure attributable to compositional sequencing. The additional signals appear as shoulders rather than as well-resolved peaks, and appear in the opposite sense to the corresponding signals in the C-13 carbonyl region, i.e., the downfield peak is BBB, the center peak is BBA + ABB, and the upfield peak is ABA. The proportions found in the several samples examined are in agreement with the results found from the C-13 spectrum of carbonyl groups.

Tin-119 NMR is better suited than proton or C-13 NMR to searching for impurities, inasmuch as common solvents are free from tin compounds. In general, all samples from whatever source have 96 percent or more of the tin signal in the region 90 to 98 ppm attributed to $-COOSnBu_3$ on the polymer chain. Samples OMP-2N and OMP-8N (fig. 10) had additional signals. The lower field signal, about 105 ppm, is tentatively attributed to tributyltin benzoate, which could arise from decomposition of the initiator, benzoyl peroxide. The rather sharp signal at 97 ppm overlapping the polymer signal (see below) arises from TBTM.

Referring again to figure 2 samples OMP-2P and OMP-8P have three impurity peaks. One, found at -12 ppm, is doubled by addition of 20 µL of tetrabutyltin (fig. 21), and is therefore attributed to that substance. A second sharp peak, about 72 ppm, is in the region given in the literature for a tributytin alkoxide [16] and may be the 4-butylcyclohexyl oxide of tributyltin. This could arise as a decomposition product of the Percadox initiator. The third impurity peak, about 112 ppm, is much broader than the two peaks at lower field and coincides with the signal from added tributyltin methoxide. The result of adding tetrabutyltin has been described above. Additions of TBTM give a fairly sharp signal about 104 ppm (figure 22) which overlaps the polymer signal to a degree and is therefore not readily quantitated. Additions of TBTO were made to sample OMP-2P in order to learn if it were responsible for the downfield peak. The first three aliquots gave no appreciable signal anywhere in the spectrum. Finally, a fourth
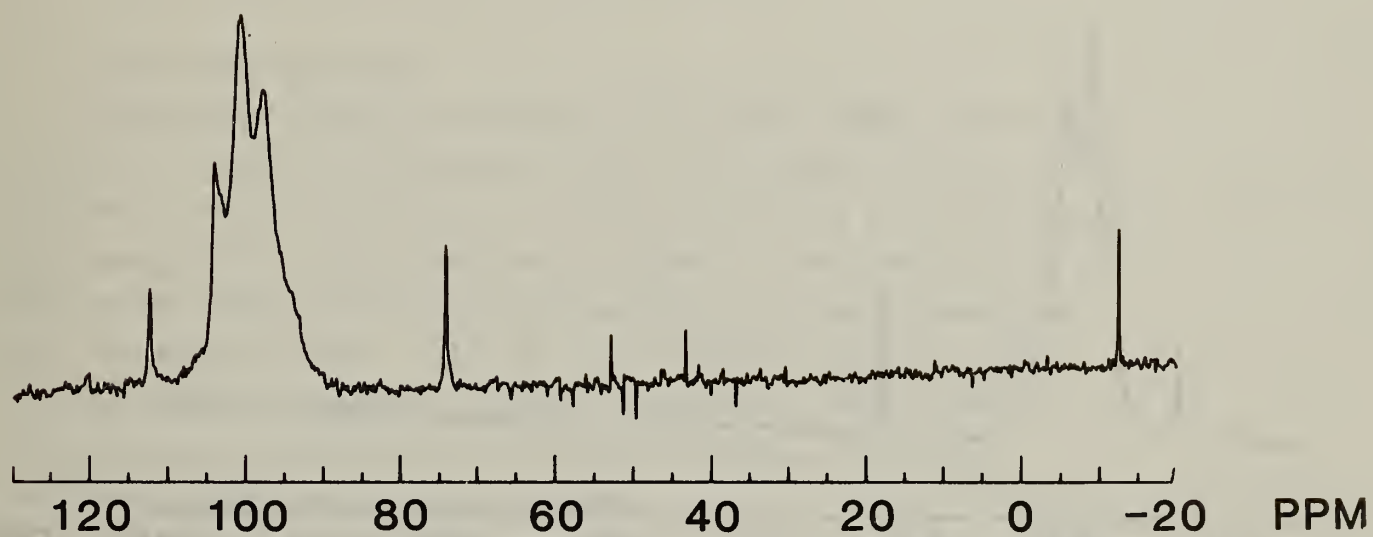
Figure 21.   Same as figure 2(A) plus 20 µl of tetrabutyltin, showing
growth of its peak at -12 ppm.
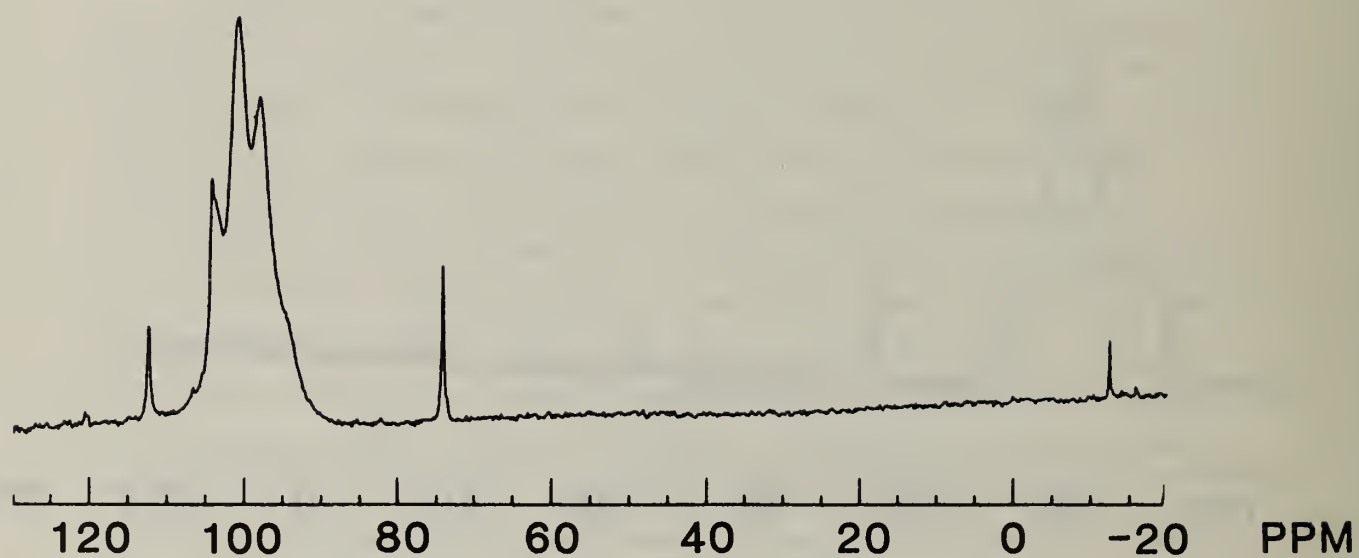
Figure 22.   Same as figure 2(A) plus 15 µL of TBTM, showing growth
of its peak at 104 ppm.

aliquot did increase the signal at 90 ppm (fig. 23). A possible explanation for this observation is that the polymer sample contains unreacted pendant free acid groups (which we are not able to detect by either proton or C-13 NMR) and that the first aliquots of TBTO were used up in reacting with these acid groupings. With the addition of tributyltin methoxide, again no signal was observed until 328 μL had been added (fig. 24). Two signals were actually observed; one corresponding to the impurity at 100 ppm while the other appeared to be TBTO at 92 ppm formed by the hydrolysis of the initial aliquots of tributyltin methoxide added. In figure 25 are shown spectra of early samples of OMP-2P(A) and OMP-2N(B). Despite the fact that preparation of OMP-2P uses no TBTM, the signal at 97 ppm in both spectra obtained from toluene solutions arises from that substance.

4.0 Summary and Conclusions

We have shown that the combination of SEC and FTNMR provides a set of powerful tools for the characterization of organotin vinyl copolymers. Direct comparison of samples prepared by esterification of prepolymer (OMP-P series) and samples prepared by copolymerization of TBTM and MMA (OMP-N series) shows essentially the same chromatograms (SEC) and spectra (NMR). There are small differences (below the 1 percent level) in impurity content as measured by Sn-119 NMR. At present these differences have not been correlated with field performance of the materials as biocides.

SEC analysis can provide a measure of molecular weight, molecular weight dispersion, and the distribution of tin among fractions of different molecular weights. This last is most important since it is known that there is a strong negative correlation between proportion of tin in the low MW material and its field performance. The lack of suitable standards means that it is not possible to determine absolute molecular weights. Nevertheless, so long as materials of similar composition are being compared, the relative molecular weights are valid and are useful for predictive purposes.

Although NMR spectra can be run on polymer solutions as received, substantially better results are obtainable with a relatively small amount of pretreatment. In the case of Sn-119 NMR, this pretreatment

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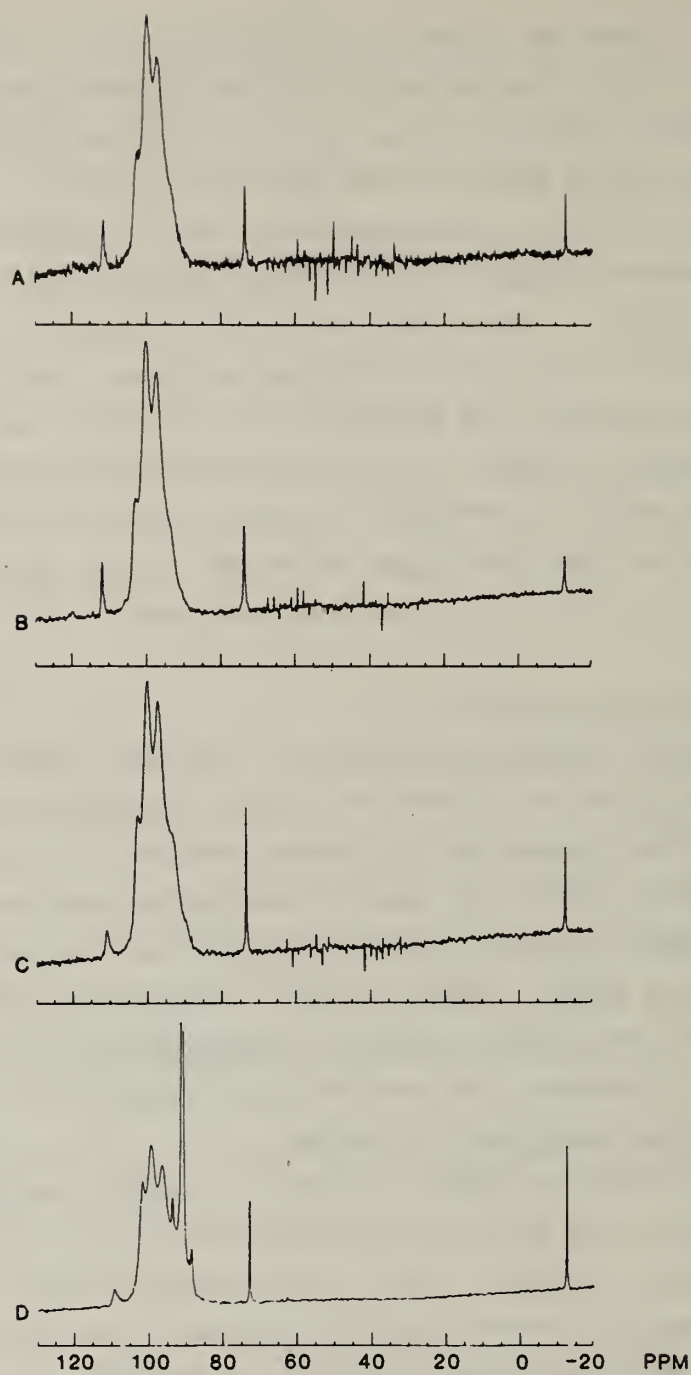
Figure 23.   Same as figure 2(A) with additions of TBTO. (A) 7.8 µL;
               (B) 78 µL; (C) 328 µL; (D) 1328 µL.

42
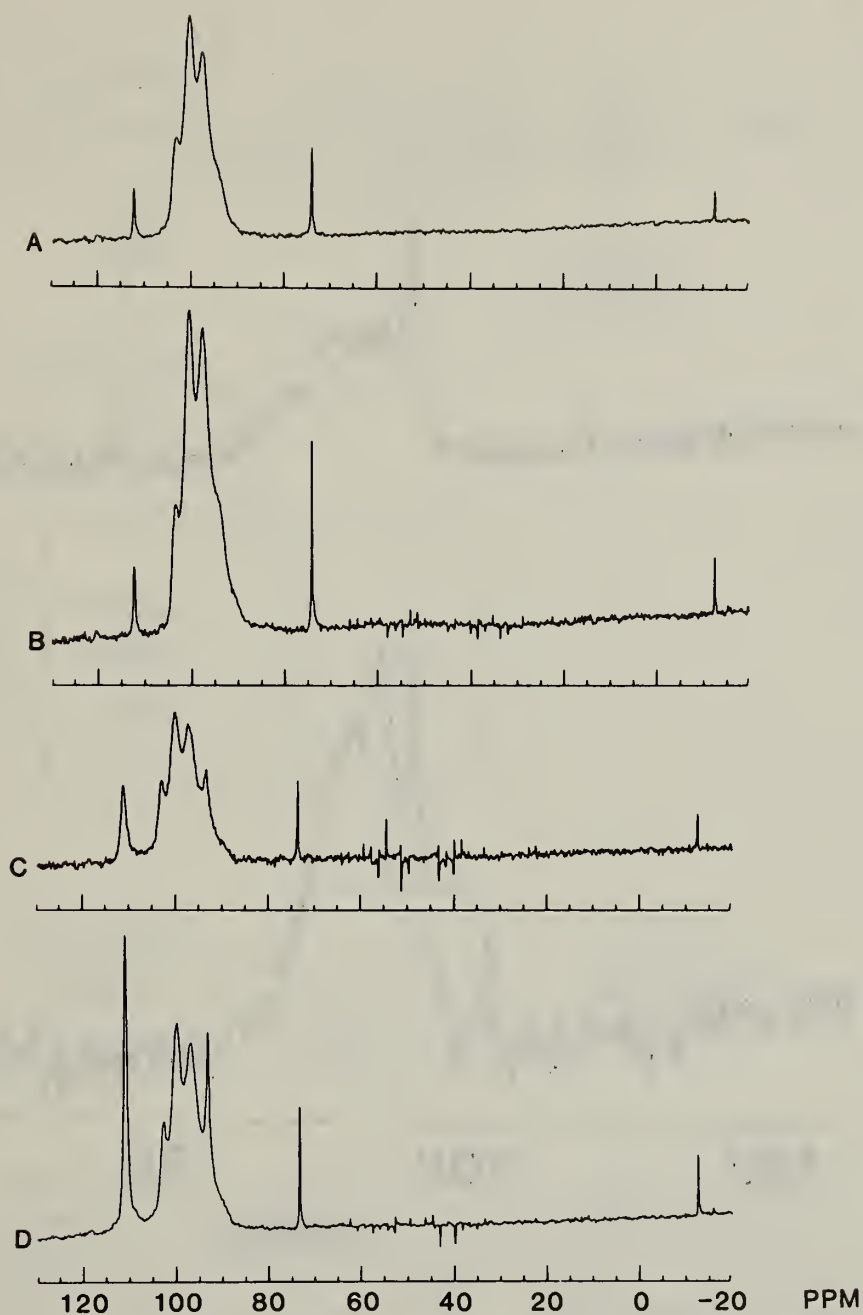
Figure 24.   Same as figure 2(A) with additions of tributyltin methoxide.
(A) 20 µL; (B) 120 µL; (C) 500 µL; (D) 750 µL.

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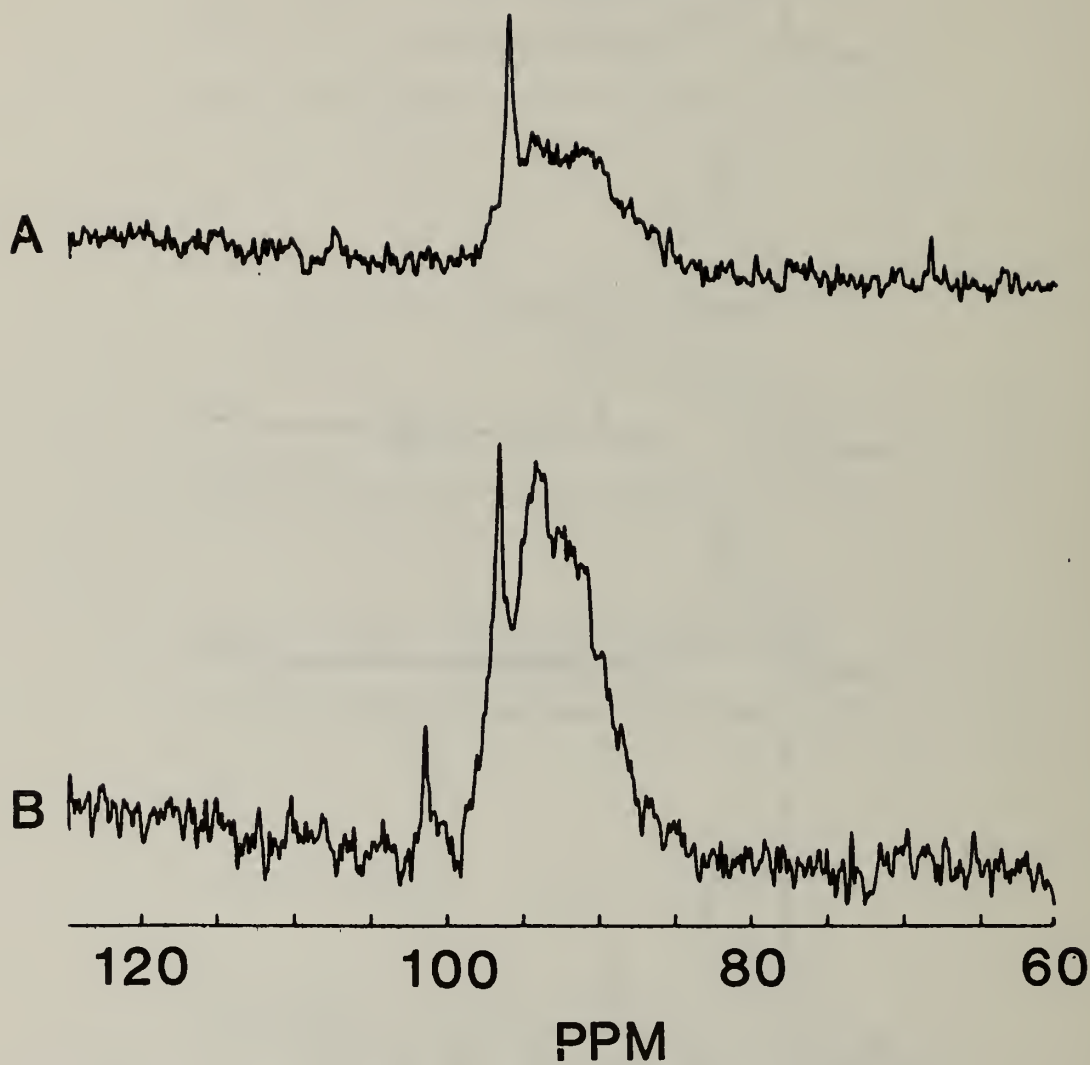
Figure 25.   Tin-119 NMR at 74.6 MHz of OMP-2 in toluene. (A) OMP-2P;
(B) OMP-2N.   The sharp peak at 97 ppm arises from TBTM.

Figure 26.   Experimental arrangements for SEC. Solvents degassed by
              stirring under partial vacuum. HPLC pumps delivered
              eluent at a controlled flow rate of 0.5 or 1.0 mL
              $min^{-1} \pm 0.001$ mL min^{-1}. Sample injection valve equipped with
              loops of 50 µL or 500 µL volume. Recommended column set
              includes at least one of pore size 10^4 Å and one of pore
              size 10^2 Å. Two or more of each size may be desired.
              UV/ΔRI detector: dual detector preferred; two detectors
              in tandem may be used, in conjunction with an automatic
              dual pen recorder. An autosampler may be used for
              on-line GFAA, or fractions may be collected for off-line
              GFAA.

consists only of diluting the polymer solution with an equal volume of $CDCl_3$. The usual tin NMR spectrum shows a triplet, not completely resolved, at about 90 to 98 ppm. The Sn-119 NMR spectrum is little affected by tacticity, and the triplet splitting is due to compositional sequencing effects. From lowest to highest field, the three peaks arise from BBB, (BBA+ABB), and ABA sequences, where B = -$COOSnR_3$ and A = -COOMe. In addition, Sn-119 NMR will show the presence of tin-containing impurities. Some which have been identified are tetrabutyltin (12 ppm), TBTO (90 ppm), TBTM (about 97 ppm, overlaps polymer signal), and tributyltin methoxide (110 ppm). In the absence of extensive field testing or a fully adequate theory of action of controlled-release polymers, it is not possible to say with certainty that any of these impurities is either beneficial or harmful to longterm field performance of the materials. However, the means to measure, and in some cases identify, tin-containing impurities is now available. For proton and C-13 NMR, it is possible to obtain much improved spectra by working with tin-free polymer, prepared by stripping the tributyltin groups with HCl and $CHCl_3$ as described above. Although proton NMR provides an a priori measure of tacticity in the CH_2 signal at 1.8 ppm, the same information can be better obtained from the carbon-13 spectrum. (In a vinyl copolymer containing a relatively small proportion of isotactic sequences, such as we have in the OMP series, the triad sequences as seen in C-13 NMR give double the signal for isotactic material compared to the dyad sequences as seen in proton NMR, for statistical reasons.)

Carbon-13 NMR gives signals from the β-methyl, quaternary, methoxyl, methylene, and carbonyl carbons which are informative to varying degrees, as discussed above. If only one signal were to be observed, it should be carbonyl since this provides (1) the ratio of -COOMe to -COOH, (2) tacticity, and (3) compositional sequencing information.

In conclusion, the combination of SEC and FTNMR provides the means to measure (1) molecular weight, (2) molecular weight dispersion, (3) percent of tin associated with low MW material, (4) tin-containing impurities, (5) monomer ratio, (6) tacticity, and (7) compositional sequencing.

5.0 Acknowledgments

For valued discussion and suggestions, the authors thank Dr. Bruce Coxon, of the National Bureau of Standards, and Prof. J. M. Bellama of the University of Maryland.

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7.0 Appendix A

7.1 Procedure for Size Exclusion Chromatography of OMPs

Dissolve in degassed, filtered reagent grade THF (9 mL) 0.1 g of OMP solids. Let the mixture stand at least overnight (12 hr) to effect dissolution of the polymer. When solution appears to be complete, filter through an organic sample clarification apparatus (0.45 μm pore size), and dilute to exactly 10 mL with THF.

Set up the size exclusion apparatus as diagrammed in figure 26. Employ an HPLC pump capable of delivering eluent at a flow rate of 0.2 to at least 3.0 mL min^{-1} with an accuracy of ±0.001 mL min^{-1}. Install HPLC injection valve capable of accommodating sample loops of 20 μL to 500 μL or greater volume. Install the 500 μL loop. Connect the injection valve to the inlet end of the conditioned SEC column set. Connect the outlet to either a ΔRI/UV dual detector or ΔRI and UV detectors in tandem. To the detector outlet, attach a length of capillary tubing sufficient to transfer effluent into collection vessels.

Set the ΔRI and UV detectors at the highest sensitivities commensurate with recorder sensitivity. Record ΔRI and UV absorbances continuously on a dual pen recorder (e.g., Perkin-Elmer Model 156). With eluent flow rate set at 0.5 mL min^{-1}, inject 500 μL of the OMP solution. Collect as a single fraction all materials eluted prior to the first ΔRI peak, in a Teflon stoppered glass vial. Subsequently collect 0.5 mL fractions (or smaller if desired) similarly to be stored in Teflon stoppered glass vials. Continue collecting sample until all ΔRI and UV activity ceases, including detection of both high-and low-MW peaks, solvent peaks, and impurities. Because sample collection will occupy the operator's full attention, repeat ΔRI and UV chromatograms at least once without collecting fractions, adjusting the pen location as necessary to keep the ΔRI record on the chart, without changing the sensitivity. UV sensitivity may be changed at any time to keep the UV chromatogram on the chart paper.

Begin measurements of tin by GFAA as soon as possible after collecting all fractions. In Teflon or polyethylene cups (previously leached overnight in 10 percent HNO$_3$ at 60 °C), dilute samples of measured volume with THF to keep GFAA absorbance readings approximately

65 percent or less and as nearly equal as possible over the entire chromatograms. Note the final dilution of each fraction. At the highest polymer concentrations, dilutions of 200 to 400 may be necessary. Take three or more replicate measurements on each fraction.

Following all of the measurements on all fractions, disconnect the injection valve from the column inlet and introduce a capillary tube leading from the injection valve into a volumetric flask (10 mL). Load the 500 μL loop with OMP solution, collect several mL of eluent, and dilute volumetrically. Introduce this diluted sample into a sample cup and measure the GFAA response, again with sufficient dilution so that the readings are of an intensity nearly equal to those obtained with the chromatographic fractions.

7.2 Calculations

To obtain sample recovery (%), calculate

$$B/A \times 100 = \% \text{ recovery}$$

$$\text{where } B = \sum_{i=n}^{i=o} v_i d_i s_i$$

$$\text{where } A = v_A d_A s_A$$

v_i = volume of individual chromatographic fractions

d_i = dilution of v_i

s_i = observed signal intensities

v_A = volume of unfractionated sample (usually 10 mL)

d_A = dilution of v_A

s_A = signal intensity observed for A

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

Continuing research into the analytical methodology for characterization of organometallic polymers (OMPs) has produced improved methods of characterization by size exclusion chromatography (SEC) and Fourier transform nuclear magnetic resonance (FTNMR). Molecular weight (MW) and MW dispersion (MWD), as well as the amount of tin associated with fractions of various MW can now be reliably determined by SEC coupled with various detectors: differential refractive index (ΔRI), ultra-violet (UV), and graphite furnace atomic absorption (GFAA) spectroscopy. Configurational sequencing in terms of both tacticity and sequencing of monomer units can be determined by FTNMR, as well as certain tin-containing impurities. Removal of tributyltin groups to produce a metal-free copolymer allows much more informative FTNMR spectra to be obtained. All of the polymers examined are approximately 80 percent racemic (r) and 20 percent meso (m) in tacticity (i.e., predominantly syndiotactic). The growing chain end in the copolymer adds either of the monomer units approximately in proportion to its instantaneous concentration in the mixture (i.e., at random).

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

C-13 NMR; differential refractive index; H-1 NMR; Mil-spec; molecular weight organometallic polymer; polydispersity; size exclusion chromatography; Sn-119 NMR tacticity; tin-specific GFAA; ultraviolet spectroscopy

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